

1 **Structurally diverse triterpenes obtained**
2 **from the fruits of *Ziziphus jujuba* Mill. as**
3 **inflammation inhibitors by NF-κB signaling**
4 **pathway**

5
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132 **S1. The NMR data of compounds 2–29**

133

134 *Lup-20 (29)-en-3-on-28-oic acid (2, purity percentage is 98.3%):* White powder;

135 ¹H NMR (CDCl₃, 500 MHz) spectroscopic data: δ 0.92, 0.99, 0.99, 1.02, 1.07, 1.70

136 (3H each, all s, H₃-26, 25, 27, 24, 23 and 29), 4.61, 4.75 (1H each, both br. s, H₂-30);

137 ¹³C NMR (CDCl₃, 125 MHz) spectroscopic data: see Tab. S1; ESI-Q-Orbitrap MS

138 *m/z* 453.33734 [M–H][–] (calcd for C₃₀H₄₇O₃, 453.33632).

139 *Betulinic acid (3, purity percentage is 99.5%):* White powder; ¹H NMR (C₅D₅N,

140 600 MHz) spectroscopic data: δ 0.84, 1.02, 1.07, 1.08, 1.23, 1.80 (3H each, all s, H₃-

141 24, 25, 26, 27, 23 and 29), 3.46 (1H, t like, *ca.* *J* = 8 Hz, H-3), 4.78, 4.95 (1H each,

142 both br. s, H₂-30); ¹³C NMR (C₅D₅N, 150 MHz) spectroscopic data: see Tab. S1; ESI-

143 Q-Orbitrap MS *m/z* 455.35287 [M–H][–] (calcd for C₃₀H₄₇O₃, 455.35197); and

144 according to our identification, the chemical shift values of C-15 and C-21 in the

145 literature were exchanged.

146 *2 α -Hydroxybetulinic acid (4, purity percentage is 99.3%):* White powder; ¹H

147 NMR (C₅D₅N, 500 MHz) spectroscopic data: δ 0.91, 1.05, 1.05, 1.06, 1.25, 1.79 (3H

148 each, all s, H₃-25, 24, 26, 27, 23 and 29), 3.38 (1H, d, *J* = 9.5 Hz, H-3), 4.08 (1H, dt, *J*

149 = 4.5, 9.5 Hz, H-2), 4.77, 4.93 (1H each, both br. s, H₂-30); ¹³C NMR (C₅D₅N, 125

150 MHz) spectroscopic data: see Tab. S1; ESI-Q-Orbitrap MS *m/z* 471.34763 [M–H][–]

151 (calcd for C₃₀H₄₇O₄, 471.34689); and according to our identification, the chemical

152 shift values of C-23 and C-27, C-25 and C-26 in the literature were exchanged.

153 *3 β ,30-Dihydroxylup-20(29)-en-28-oic acid (5, purity percentage is 93.0%):*

154 White powder; ^1H NMR (DMSO- d_6 , 500 MHz) spectroscopic data: δ 0.65, 0.76, 0.87,
155 0.93, 1.24 (3H each, all s, H₃-24, 25, 26, 27 and 23), 2.97 (1H, t like, *ca.* J = 8 Hz, H-
156 3), 3.89 (2H, s, H₂-29), 4.77, 4.86 (1H each, both br. s, H₂-30); ^{13}C NMR (DMSO- d_6 ,
157 125 MHz) spectroscopic data: see Tab. S1; ESI-Q-Orbitrap MS m/z 471.34747 [M-
158 H]⁻ (calcd for C₃₀H₄₇O₄, 471.34689).

159 *2-O-trans-p-Coumaroylaliphitolic acid (6, purity percentage is 97.9%)*: White
160 powder; ^1H NMR (C₅D₅N, 500 MHz) spectroscopic data: δ 1.01, 1.04, 1.09, 1.11,
161 1.30, 1.88 (3H each, all s, H₃-25, 26, 27, 24, 23 and 29), 3.66 (1H, d, J = 10.0 Hz, H-
162 3), 4.81, 4.96 (1H each, both br. s, H₂-29), 5.65 (1H, dt, J = 4.5, 10.0 Hz, H-2), 6.63,
163 8.03 (1H each, both d, J = 16.5 Hz, H-8',7'), 7.17 (2H, d, J = 8.5 Hz, H-3',5'), 7.51
164 (2H, d, J = 8.5 Hz, H-2',6'); ^{13}C NMR (C₅D₅N, 125 MHz) spectroscopic data: see Tab.
165 S1; ESI-Q-Orbitrap MS m/z 617.38452 [M-H]⁻ (calcd for C₃₉H₅₃O₆, 617.38367).

166 *3-O-cis-p-Coumaroylaliphitolic acid (7, purity percentage is 97.3%)*: White
167 powder; ^1H NMR (C₅D₅N, 600 MHz) spectroscopic data: δ [1.32 (1H, t, J = 10.8 Hz),
168 2.37 (1H, dd, J = 4.2, 10.8 Hz), H₂-1], 4.26 (1H, dt, J = 4.2, 10.8 Hz, H-2), 5.20 (1H,
169 d, J = 10.8 Hz, H-3), 1.03 (1H, m, overlapped, H-5), [1.35, 1.45 (1H, both m,
170 overlapped), H₂-6], [1.32 (1H, m), 1.35 (1H, m, overlapped), H₂-7], 1.45 (1H, m,
171 overlapped, H-9), 1.21, 1.50 (1H each, both m, H₂-11), 1.20, 1.92 (1H each, both m,
172 H₂-12), 2.72 (1H, dt, J = 3.0, 11.4 Hz, H-13), 1.22, 1.85 (1H each, both m, H₂-15),
173 [1.55 (1H, m), 2.63 (1H, dt, J = 3.0, 12.6 Hz), H₂-16], 1.74 (1H, t like, *ca.* J = 11 Hz,
174 H-18), 3.53 (1H, dt, J = 4.2, 10.8 Hz, H-19), 1.53, 2.23 (2H, m, H₂-21), 1.60, 2.25
175 (1H each, both m, H₂-22), 1.03, 0.96, 0.89, 1.03, 1.04, 1.78 (3H each, all s, H₃-23, 24,

176 25, 26, 27 and 29), 4.71, 4.94 (1H each, both br. s, H₂-30), 8.15 (2H, d, *J* = 8.5 Hz, H-
177 2',6'), 7.14 (2H, d, *J* = 8.5 Hz, H-3',5'), 6.93, 6.09 (1H each, both d, *J* = 12.6 Hz, H-
178 7', 8'); ¹³C NMR (C₅D₅N, 150 MHz) spectroscopic data: see Tab. S1; ESI-Q-Orbitrap
179 MS *m/z* 617.38422 [M-H]⁻ (calcd for C₃₉H₅₃O₆, 617.38367).

180 (3 α ,4 β ,5 β ,8 α ,9 β ,10 α ,13 α ,14 β ,15 β)-13-Carboxy-4,9-dimethyl-15-(1-
181 methylethenyl)-3-(1-methylethyl)-18-norandrostane-4-propanoic acid (**8**, purity
182 percentage is 96.5%): White powder; ¹H NMR (C₅D₅N, 600 MHz) spectroscopic data:
183 δ 1.97 (2H, m, overlapped, H₂-1), 2.51 (2H, t, *J* = 7.8 Hz, H₂-2), 1.94 (1H, m, H-4),
184 1.18 (1H, m, overlapped, H-5), 1.33 (2H, m, H₂-6), 1.36, 1.42 (1H each, both m, H₂-
185 7), 1.72 (1H, br. d, *ca.* *J* = 12 Hz, H-9), 1.18, 1.54 (1H each, both m, overlapped, H₂-
186 11), 1.24, 1.94 (1H each, both m, H₂-13), 2.79 (1H, t like, *ca.* *J* = 11 Hz, H-14), 1.27,
187 1.84 (1H each, both m, H₂-15), 1.55, 2.63 (1H each, both m, H₂-16), 1.79 (1H, m,
188 overlapped, H-18), 3.55 (1H, t like, *ca.* *J* = 11 Hz, H-19), 1.53, 2.25 (2H, m, H₂-21),
189 1.57, 2.28 (1H each, both m, H₂-22), 0.94, 0.76, 0.79, 1.07, 1.12, 1.79 (3H each, all s,
190 H₃-23, 24, 25, 26, 27 and 29), 4.78, 4.96 (1H each, both s, H₂-30); ¹³C NMR (C₅D₅N,
191 150 MHz) spectroscopic data: see Tab. S1; ESI-Q-Orbitrap MS *m/z* 471.34756 [M-
192 H]⁻ (calcd for C₃₀H₄₇O₄, 471.34689).

193 *Ceanothic acid* (**9**, purity percentage is 99.0%): White powder; ¹H NMR (C₅D₅N,
194 500 MHz) spectroscopic data: δ 1.08, 1.16, 1.27, 1.40, 1.43, 1.67 (3H each, all s, H₃-
195 27, 26, 24, 25, 23 and 29), 4.67, 4.86 (1H each, both s, H₂-30); ¹³C NMR (C₅D₅N, 125
196 MHz) spectroscopic data: see Tab. S1; ESI-Q-Orbitrap MS *m/z* 485.32706 [M-H]⁻
197 (calcd for C₃₀H₄₅O₅, 485.32615). And according to our identification, the chemical

198 shift values of C-4 and C-8 in the literature were exchanged.

199 *Ceanothic acid 2-methyl ester (10, purity percentage is 98.2%)*: White powder;
200 ¹H NMR (C₅D₅N, 600 MHz) spectroscopic data: δ 1.11, 1.14, 1.22, 1.31, 1.33, 1.78
201 (3H each, all s, H₃-26, 27, 24, 25, 23 and 29), 3.01 (1H, br. s, H-1), 4.60 (1H, br. s, H-
202 3), 4.74, 4.95 (1H each, both s, H₂-30); ¹³C NMR (C₅D₅N, 150 MHz) spectroscopic
203 data: see Tab. S1; ESI-Q-Orbitrap MS *m/z* 499.34256 [M-H]⁻ (calcd for C₃₁H₄₇O₅,
204 499.3418).

205 *3-Oxo-oleana-12-en-28-oic acid (11, purity percentage is 96.3%)*: White powder;
206 ¹H NMR (C₅D₅N, 500 MHz) spectroscopic data: δ 0.90, 0.97, 1.01, 1.02, 1.02, 1.16,
207 1.26 (3H each, all s, H₃-25, 29, 26, 24, 30, 23 and 27), 5.50 (1H, br. s, H-12); ¹³C
208 NMR (C₅D₅N, 125 MHz) spectroscopic data: see Tab. S1; ESI-Q-Orbitrap MS *m/z*
209 453.33710 [M-H]⁻ (calcd for C₃₀H₄₅O₃, 453.33632). And according to our
210 identification, the chemical shift values of C-9 and C-17 in the literature were
211 exchanged.

212 *Oleanolic acid (12, purity percentage is 94.9%)*: White powder; ¹H NMR
213 (C₅D₅N, 600 MHz) spectroscopic data: δ 0.91, 0.97, 1.03, 1.04, 1.04, 1.26, 1.30 (3H
214 each, all s, H₃-25, 29, 30, 24, 26, 23 and 27), 3.46 (1H, dd, *J* = 4.8, 10.2 Hz, H-3),
215 5.52 (1H, t, *J* = 3.6 Hz, H-12); ¹³C NMR (C₅D₅N, 150 MHz) spectroscopic data: see
216 Tab. S2; ESI-Q-Orbitrap MS *m/z* 455.35303 [M-H]⁻ (calcd for C₃₀H₄₇O₃, 455.35197).

217 *Maslinic acid (13, purity percentage is 97.3%)*: White powder; ¹H NMR (C₅D₅N,
218 500 MHz) spectroscopic data: δ 0.95, 0.99, 1.01, 1.01, 1.07, 1.27, 1.27 (3H each, all s,
219 H₃-29, 25, 26, 30, 24, 23 and 27), 3.38 (1H, d, *J* = 9.5 Hz, H-3), 4.07 (1H, ddd, *J* = 4.5,

220 10.0, 14.0 Hz, H-2), 5.46 (1H, t, $J = 4.0$ Hz, H-12); ^{13}C NMR ($\text{C}_5\text{D}_5\text{N}$, 125 MHz)
221 spectroscopic data: see Tab. S2; ESI-Q-Orbitrap MS m/z 471.34799 $[\text{M}-\text{H}]^-$ (calcd
222 for $\text{C}_{30}\text{H}_{47}\text{O}_4$, 471.34689). And according to our identification, the chemical shift
223 values of C-1 and C-17 in the literature were exchanged.

224 *11-Oxo-maslinic acid (2 α ,3 β -dihydroxy-11-oxo-18 β -olean-12-en-28-oic acid (14,*
225 *purity percentage is 98.0%):* White powder; ^1H NMR (CD_3OD , 600 MHz)
226 spectroscopic data: δ 0.81, 0.94, 0.96, 0.98, 1.02, 1.17, 1.41 (3H each, all s, H₃-24, 29,
227 30, 26, 23, 25 and 27), 2.92 (1H, d, $J = 9.6$ Hz, H-3), 3.67 (1H, ddd, $J = 4.2, 9.6, 14.4$
228 Hz, H-2), 5.56 (1H, s, H-12); ^{13}C NMR (CD_3OD , 150 MHz) spectroscopic data: see
229 Tab. S2; ESI-Q-Orbitrap MS m/z 485.32717 $[\text{M}-\text{H}]^-$ (calcd for $\text{C}_{30}\text{H}_{45}\text{O}_5$, 485.32615).
230 And according to our identification, the chemical shift values of C-7 and C-22 in the
231 literature were exchanged.

232 *2 α -trans-p-Coumaroyloxy-2 α ,3 β ,23 α -trihydroxy-olean-12-en-28-oic acid (15,*
233 *purity percentage is 91.5%):* White powder; ^1H NMR ($\text{DMSO}-d_6$, 600 MHz)
234 spectroscopic data: δ 0.72, 0.77, 0.87, 0.87, 0.96, 0.99, 1.10 (3H each, all s, H₃-26, 24,
235 29, 30, 23, 25 and 27), 3.13 (1H, d, $J = 10.8$ Hz, H-3), 4.90 (1H, dt, *ca.* $J = 4.8, 10.8$
236 Hz, H-2), 5.17 (1H, br. s, H-12), 6.32, 7.54 (1H each, both d, $J = 15.6$ Hz, H-8',7'),
237 6.80 (2H, d, $J = 8.4$ Hz, H-3',5'), 7.52 (2H, d, $J = 8.4$ Hz, H-2',6'); ^{13}C NMR ($\text{DMSO}-$
238 d_6 , 150 MHz) spectroscopic data: see Tab. S2; ESI-Q-Orbitrap MS m/z 617.38428
239 $[\text{M}-\text{H}]^-$ (calcd for $\text{C}_{39}\text{H}_{53}\text{O}_6$, 617.38367).

240 *2 α -cis-p-Coumaroyloxy-2 α ,3 β ,23 α -trihydroxy-olean-12-en-28-oic acid (16,*
241 *purity percentage is 98.0%):* White powder; ^1H NMR ($\text{DMSO}-d_6$, 600 MHz)

242 spectroscopic data: δ 0.72, 0.77, 0.87, 0.87, 0.98, 0.99, 1.10 (3H each, all s, H₃-26, 24,
243 29, 30, 23, 25 and 27), 3.13 (1H, d, J = 10.8 Hz, H-3), 4.90 (1H, dt, *ca.* J = 4.8, 10.8
244 Hz, H-2), 5.14 (1H, br. s, H-12), 5.75, 6.81 (1H each, both d, J = 13.2 Hz, H-8',7'),
245 6.75 (2H, d, J = 8.4 Hz, H-3',5'), 7.69 (2H, d, J = 8.4 Hz, H-2',6'); ¹³C NMR (DMSO-
246 *d*₆, 150 MHz) spectroscopic data: see Tab. S2; ESI-Q-Orbitrap MS m/z 617.38440
247 [M-H]⁻ (calcd for C₃₉H₅₃O₆, 617.38367).

248 *3-O-trans-p-Coumaroyl maslinic acid (17, purity percentage is 98.0%)*: White
249 powder; ¹H NMR (C₅D₅N, 600 MHz) spectroscopic data: δ 0.97, 1.01, 1.01, 1.02,
250 1.04, 1.06, 1.28 (3H each, all s, H₃-29, 25, 26, 30, 24, 23 and 27), 4.29 (1H, ddd, J =
251 4.8, 10.2, 10.8 Hz, H-2), 5.24 (1H, d, J = 10.2 Hz, H-3), 5.47 (1H, br. s, H-12), 6.68,
252 8.00 (1H each, both d, J = 15.6 Hz, H-8',7'), 7.16 (2H, d, J = 8.4 Hz, H-3',5'), 7.56
253 (2H, d, J = 8.4 Hz, H-2',6'); ¹³C NMR (C₅D₅N, 150 MHz) spectroscopic data: see Tab.
254 S2; ESI-Q-Orbitrap MS m/z 617.38403 [M-H]⁻ (calcd for C₃₉H₅₃O₆, 617.38367).

255 *3,4-Seco-olean-12-ene-3,28-dioic acid (18, purity percentage is 98.3%)*: White
256 powder; ¹H NMR (C₅D₅N, 600 MHz) spectroscopic data: δ 0.77, 0.85, 0.95, 0.99,
257 1.02, 1.03, 1.26 (3H each, all s, H₃-24, 25, 23, 29, 30, 26 and 27), 5.49 (1H, br. s, H-
258 12); ¹³C NMR (C₅D₅N, 150 MHz) spectroscopic data: see Tab. S2; ESI-Q-Orbitrap
259 MS m/z 471.34741 [M-H]⁻ (calcd for C₃₀H₄₇O₄, 471.34689).

260 *3-Oxo-urs-12-en-28-oic acid (19, purity percentage is 96.5%)*: White powder;
261 ¹H NMR (C₅D₅N, 600 MHz) spectroscopic data: δ 0.89, 1.00, 1.02, 1.14, 1.20 (3H
262 each, all s, H₃-25, 24, 26, 23 and 27), 0.97 (3H, d, J = 6.0 Hz, H₃-30), 1.00 (1H, d, J =
263 6.0 Hz, H₃-29), 5.47 (1H, br. s, H-12); ¹³C NMR (C₅D₅N, 150 MHz) spectroscopic

264 data: see Tab. S2; ESI-Q-Orbitrap MS m/z 453.33716 $[M-H]^-$ (calcd for $C_{30}H_{45}O_3$,
265 453.33632).

266 *Ursolic acid (20, purity percentage is 95.3%)*: White powder; 1H NMR (C_5D_5N ,
267 600 MHz) spectroscopic data: δ 0.91, 1.04, 1.07, 1.24, 1.26 (3H each, all s, H_3 -25, 24,
268 26, 27 and 23), 0.97 (3H, d, $J = 6.6$ Hz, H_3 -30), 1.02 (1H, d, $J = 6.6$ Hz, H_3 -29), 3.47
269 (1H, dd, $J = 5.4, 10.2$ Hz, H-3), 5.51 (1H, t, $J = 3.0$ Hz, H-12); ^{13}C NMR (C_5D_5N , 150
270 MHz) spectroscopic data: see Tab. S3; ESI-Q-Orbitrap MS m/z 455.35297 $[M-H]^-$
271 (calcd for $C_{30}H_{47}O_3$, 455.35197).

272 *2 α -Hydroxyursolic acid (21, purity percentage is 95.3%)*: White powder; 1H
273 NMR (C_5D_5N , 500 MHz) spectroscopic data: δ 0.97, 1.03, 1.06, 1.21, 1.26 (3H each,
274 all s, H_3 -25, 26, 24, 27 and 23), 0.96 (3H, d, $J = 6.5$ Hz, H_3 -30), 0.99 (1H, d, $J = 6.5$
275 Hz, H_3 -29), 3.38 (1H, d, $J = 9.5$ Hz, H-3), 4.07 (1H, ddd, $J = 4.5, 9.5, 14.0$ Hz, H-2),
276 5.47 (1H, t, $J = 3.5$ Hz, H-12); ^{13}C NMR (C_5D_5N , 125 MHz) spectroscopic data: see
277 Tab. S3; ESI-Q-Orbitrap MS m/z 471.34784 $[M-H]^-$ (calcd for $C_{30}H_{47}O_4$, 471.34689).

278 *Jacoumaric acid (22, purity percentage is 93.0%)*: White powder; 1H NMR
279 (C_5D_5N , 500 MHz) spectroscopic data: δ 0.97 (3H, d, $J = 6.0$ Hz, H_3 -30), 1.00 (3H, d,
280 $J = 5.0$ Hz, H_3 -29), 1.01, 1.05, 1.05, 1.09, 1.24 (3H each, all s, H_3 -25, 24, 26, 23 and
281 27), 4.29 (1H, dt, $J = 5.0, 9.5$ Hz, H-2), 5.27 (1H, d, $J = 9.5$ Hz, H-3), 5.48 (1H, t, $J =$
282 4.0 Hz, H-12), 6.68, 8.00 (1H each, both d, $J = 16.0$ Hz, H-8',7'), 7.17 (2H, d, $J = 8.5$
283 Hz, H-3',5'), 7.51 (2H, d, $J = 8.5$ Hz, H-2',6'); ^{13}C NMR (C_5D_5N , 125 MHz)
284 spectroscopic data: see Tab. S3; ESI-Q-Orbitrap MS m/z 617.38409 $[M-H]^-$ (calcd
285 for $C_{39}H_{53}O_6$, 617.38367). And according to our identification, the chemical shift

286 values of C-26 and C-29, C-3',5' and C-8' in the literature were exchanged.

287 *(1S,2S,4aR,4bS,6aS,9R,10S,10aS,12aR)-6a-Carboxy-*
288 *1,2,3,4,4a,4b,5,6,6a,7,8,9,10,10a,12,12a-hexadecahydro-1,4a,4b,9,10-pentamethyl-2-*
289 *(1-methylethyl)-1-chrysenepropanoic acid (23, purity percentage is 92.8%):* White
290 powder; ¹H NMR (C₅D₅N, 600 MHz) spectroscopic data: δ 1.99 (2H, m, overlapped,
291 H₂-1), 2.53 (2H, t, *J* = 7.2 Hz, H₂-2), 1.92 (1H, m, H-4), 1.22 (1H, m, overlapped, H-
292 5), 1.35 (1H, m, H₂-6), 1.38, 1.46 (1H each, both m, H₂-7), 2.01 (1H, m, overlapped,
293 H-9), 1.95, 2.09 (1H each, both m, H₂-11), 5.48 (1H, t like, *ca.* *J* = 4 Hz, H-12), [1.23
294 (1H, m, overlapped), 2.31 (1H, br. t, *ca.* *J* = 11 Hz), H₂-15], 2.07, 2.12 (1H each, both
295 m, H₂-16), 2.64 (1H, d, *J* = 10.2 Hz, H-18), 1.45 (1H, m, H-19), 1.02 (1H, m, H-20),
296 2.00 (2H, m, overlapped, H₂-21), 1.37, 1.47 (1H each, both m, H₂-22), 0.93, 0.77,
297 0.85, 1.07, 1.24 (3H each, all s, H₃-23, 24, 25, 26 and 27), 0.94, 0.95 (3H each, both d,
298 *J* = 6.0 Hz, H₃-29 and 30); ¹³C NMR (C₅D₅N, 150 MHz) spectroscopic data: see Tab.
299 S3; ESI-Q-Orbitrap MS *m/z* 471.34763 [M-H]⁻ (calcd for C₃₀H₄₇O₄, 471.34689).

300 *Pomonic acid (24, purity percentage is 93.3%):* White powder; ¹H NMR (C₅D₅N,
301 600 MHz) spectroscopic data: δ 0.93, 1.02, 1.10, 1.15, 1.71 (3H each, all s, H₃-25, 24,
302 26, 23 and 27), 1.14 (3H, d, *J* = 6.6 Hz, H₃-30), 5.61 (1H, br. s, H-12); ¹³C NMR
303 (C₅D₅N, 150 MHz) spectroscopic data: see Tab. S3; ESI-Q-Orbitrap MS *m/z*
304 469.33218 [M-H]⁻ (calcd for C₃₀H₄₅O₄, 469.33124). And according to our
305 identification, the chemical shift values of C-23 and C-29 in the literature were
306 exchanged.

307 *Pomolic acid (25, purity percentage is 93.7%):* White powder; ¹H NMR (C₅D₅N,

308 600 MHz) spectroscopic data: δ 0.94, 1.05, 1.13, 1.26, 1.75 (3H each, all s, H₃-25, 24,
309 26, 23 and 27), 1.14 (3H, d, $J = 6.0$ Hz, H₃-30), 3.46 (1H, br. d, *ca.* $J = 9$ Hz, H-3),
310 5.63 (1H, br. s, H-12); ¹³C NMR (C₅D₅N, 150 MHz) spectroscopic data: see Tab. S3;
311 ESI-Q-Orbitrap MS m/z 471.34744 [M-H]⁻ (calcd for C₃₀H₄₇O₄, 471.34689).

312 *2-Oxopomolic acid (26, purity percentage is 93.3%)*: White powder; ¹H NMR
313 (C₅D₅N, 600 MHz) spectroscopic data: δ 0.88, 0.89, 1.06, 1.33, 1.76 (3H each, all s,
314 H₃-24, 26, 25, 23 and 27), 1.14 (3H, d, $J = 6.6$ Hz, H₃-30), 1.44 (3H, s, H₃-29), 4.20
315 (1H, s, H-3), 5.58 (1H, t, $J = 3.6$ Hz, H-12); ¹³C NMR (C₅D₅N, 150 MHz)
316 spectroscopic data: see Tab. S3; ESI-Q-Orbitrap MS m/z 485.32736 [M-H]⁻ (calcd
317 for C₃₀H₄₅O₅, 485.32615). And the chemical shift value of C-11 in the literature was
318 revised here.

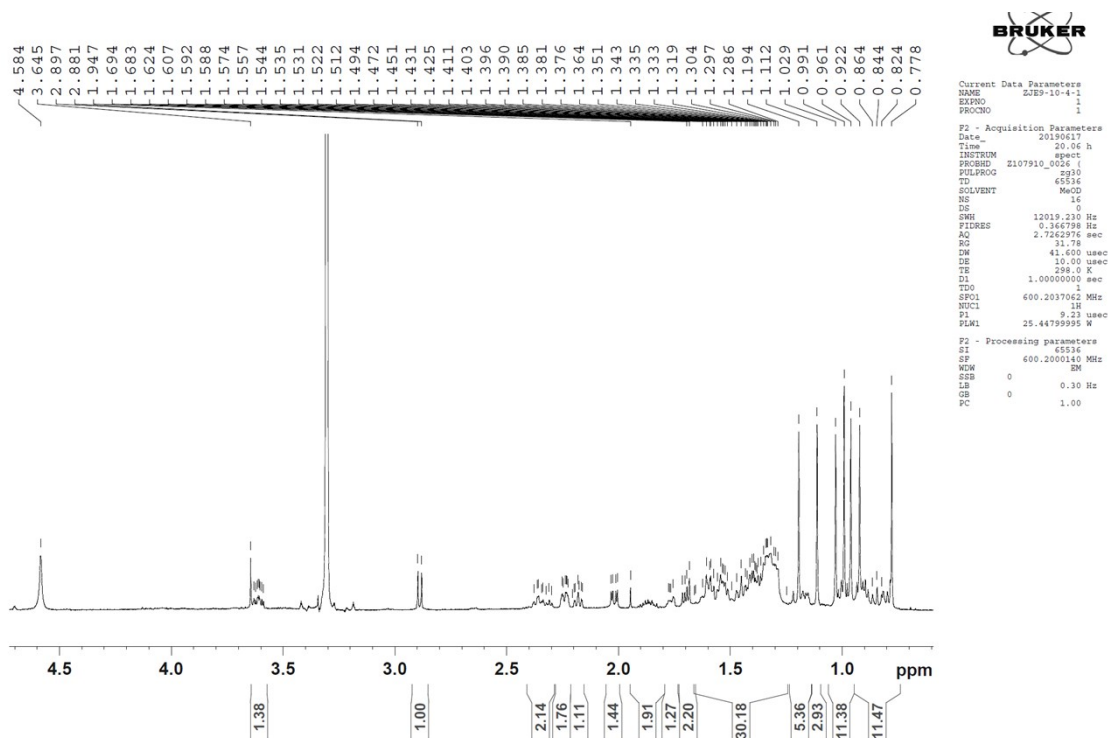
319 *Euscaphic acid (27, purity percentage is 98.3%)*: White powder; ¹H NMR
320 (C₅D₅N, 500 MHz) spectroscopic data: δ 0.92, 0.99, 1.12, 1.29, 1.66 (3H each, all s,
321 H₃-24, 25, 26, 23 and 27), 1.13 (3H, d, $J = 6.5$ Hz, H₃-30), 3.79 (1H, d, $J = 2.5$ Hz, H-
322 3), 4.33 (1H, dt, $J = 2.5, 11.0$ Hz, H-2), 5.60 (1H, br. s, H-12); ¹³C NMR (C₅D₅N, 125
323 MHz) spectroscopic data: see Tab. S3; ESI-Q-Orbitrap MS m/z 487.34286 [M-H]⁻
324 (calcd for C₃₀H₄₇O₅, 487.34180).

325 *2 β ,19 α -Hydroxyursolic acid (28, purity percentage is 97.0%)*: White powder; ¹H
326 NMR (C₅D₅N, 500 MHz) spectroscopic data: δ 1.15 (3H, d, $J = 6.5$ Hz, H₃-30), 1.19,
327 1.29, 1.41, 1.56, 1.79 (3H each, all s, H₃-26, 23, 24, 25 and 27), 1.49 (3H, s, H₃-29),
328 3.45 (1H, d, $J = 3.0$ Hz, H-3), 4.44 (1H, q, $J = 3.0$ Hz, H-2), 5.63 (1H, br. d, *ca.* $J = 4$
329 Hz, H-12); ¹³C NMR (C₅D₅N, 125 MHz) spectroscopic data: see Tab. S3; ESI-Q-

330 Orbitrap MS m/z 487.34277 $[M-H]^-$ (calcd for $C_{30}H_{47}O_5$, 487.34180). And the
331 chemical shift value of C-2 in the literature was revised here.

332 *Cecropiacic acid (29, purity percentage is 99.0%)*: White powder; 1H NMR
333 (C_5D_5N , 600 MHz) spectroscopic data: δ 1.09 (3H, d, $J = 6.6$ Hz, H₃-30), 1.19, 1.20,
334 1.36, 1.56, 1.59, 1.88 (3H each, all s, H₃-26, 25, 29, 23, 24 and 27), 5.66 (1H, t like,
335 *ca.* $J = 4$ Hz, H-12); ^{13}C NMR (C_5D_5N , 150 MHz) spectroscopic data: see Tab. S3;
336 ESI-Q-Orbitrap MS m/z 517.31659 $[M-H]^-$ (calcd for $C_{30}H_{45}O_7$, 517.31598).
337 According to our identification, the chemical shift values of H₃-23 and H₃-24 in the
338 literature were exchanged.

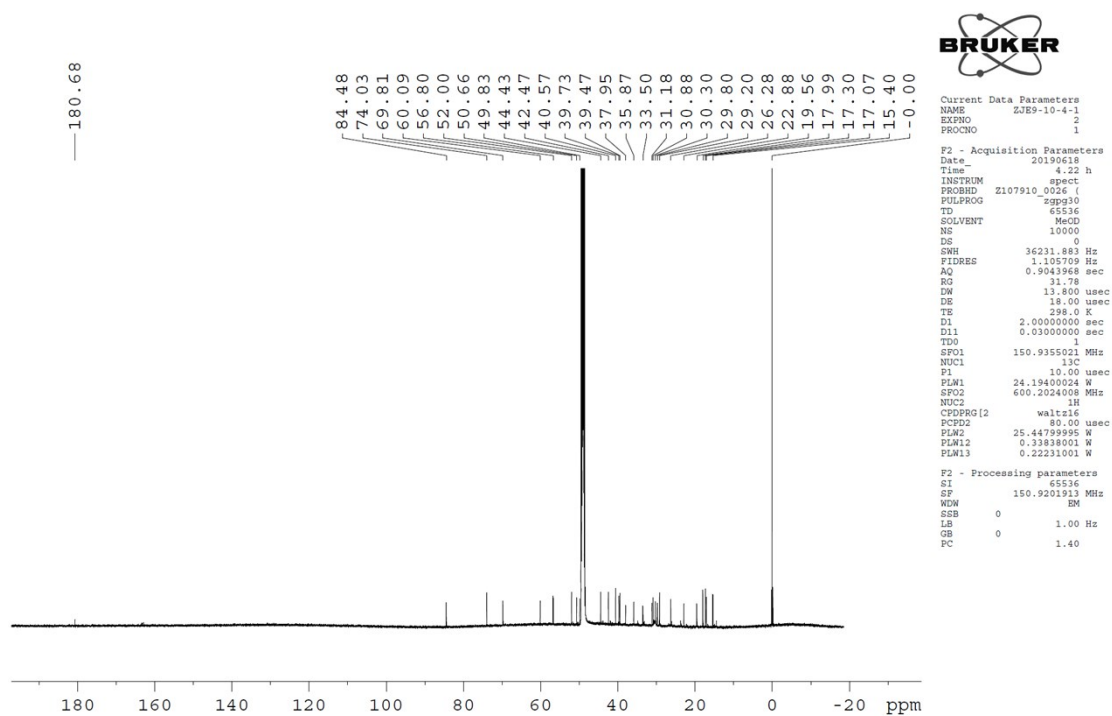
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Fig. S1. ¹H NMR (600MHz, CD₃OD) spectrum of compound 1

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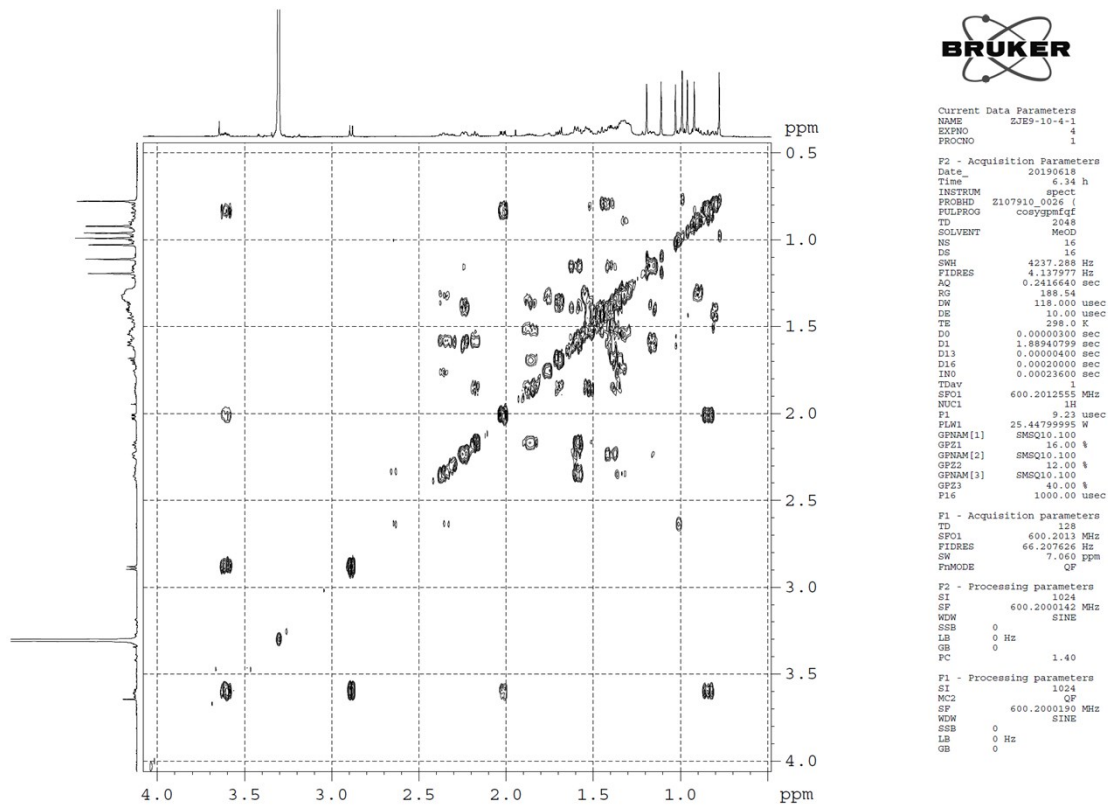
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Fig. S2. ¹³C NMR (150MHz, CD₃OD) spectrum of compound 1

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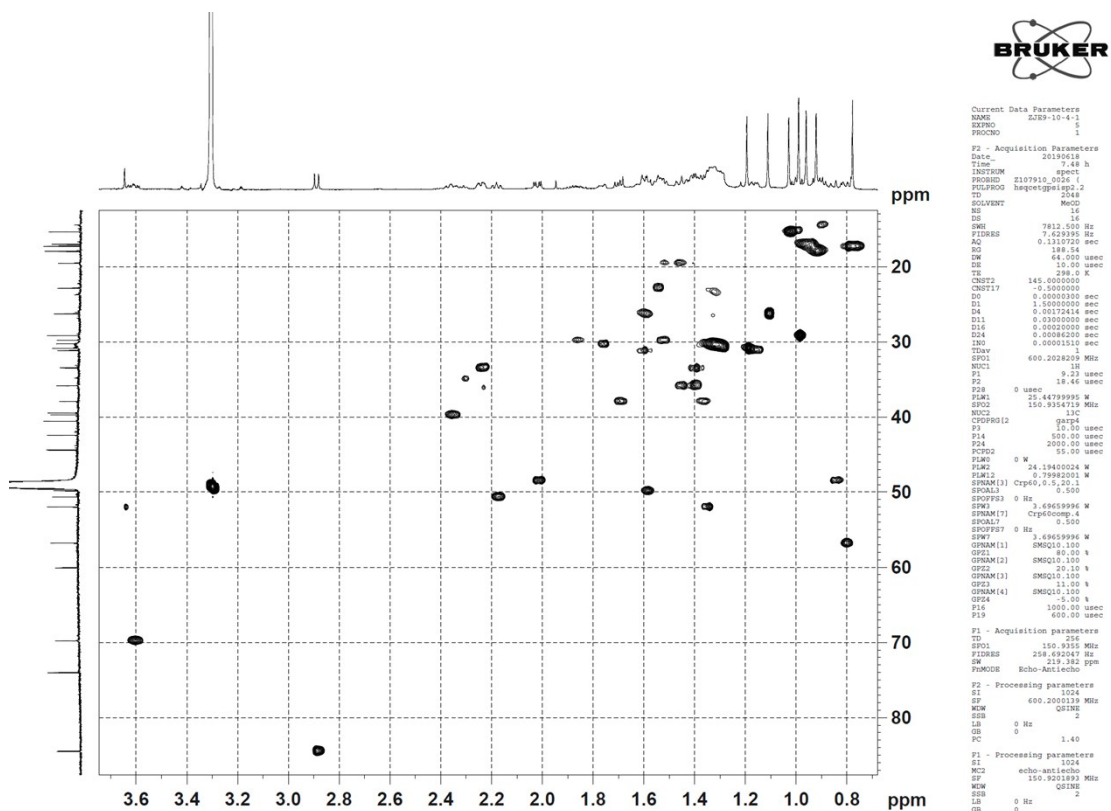


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Fig. S3. The ^1H ^1H COSY (CD_3OD) spectrum of compound 1

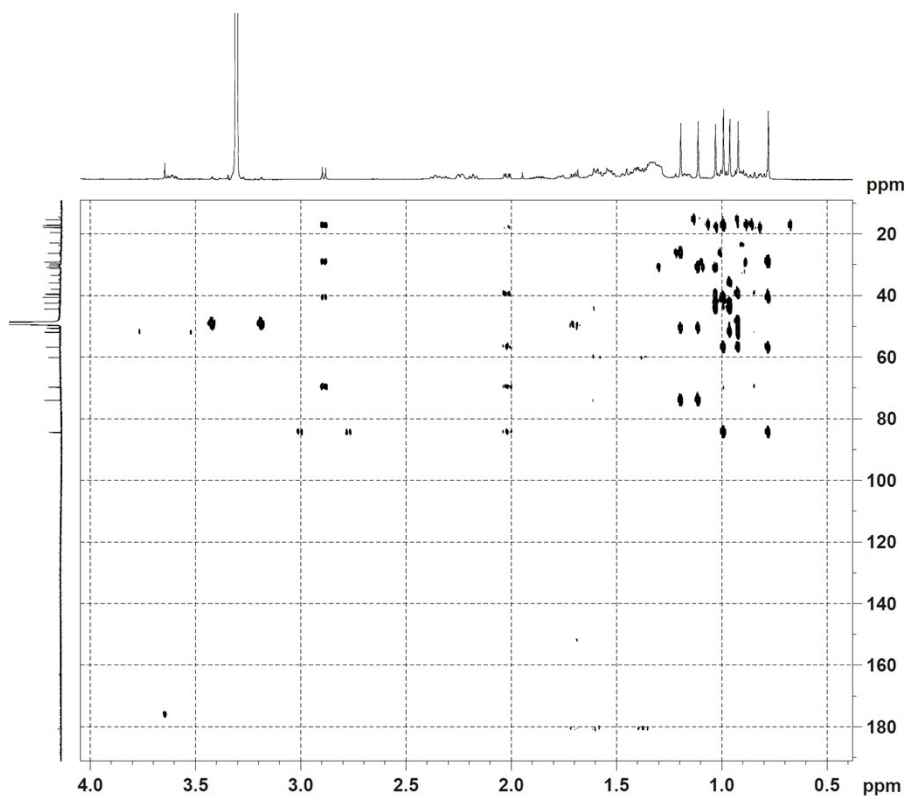


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Fig. S4. The HSQC (CD_3OD) spectrum of compound 1



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EXPNO    12
PROCNO   1

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PULPROG  hmcgprndgdf
TD        4096
SOLVENT  MeOD
NS        100
DS        16
SWH       3906.250 Hz
FIDRES   1.897349 Hz
AQ        0.5242880 sec
RG        188.54
DW        128.000 usec
DE        10.00 usec
TE        298.0 K
CNS113   8.0000000
DO        0.0000000 sec
D1        1.23785603 sec
D2        0.04620000 sec
D16       0.00020000 sec
INO       0.00001510 sec
TD0AV    1
SF01     600.2014707 MHz
NUC1      1H
P1        9.23 usec
P2        18.46 usec
PLW1     25.44799995 W
SF02     150.9355021 MHz
NUC2      13C
P3        10.00 usec
PLW2     24.39400024 W
GPNAM[1] SMSQ10.100
GP21     50.00 %
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GPNAM[3] SMSQ10.100
GP23     40.10 %
P16      1000.00 usec

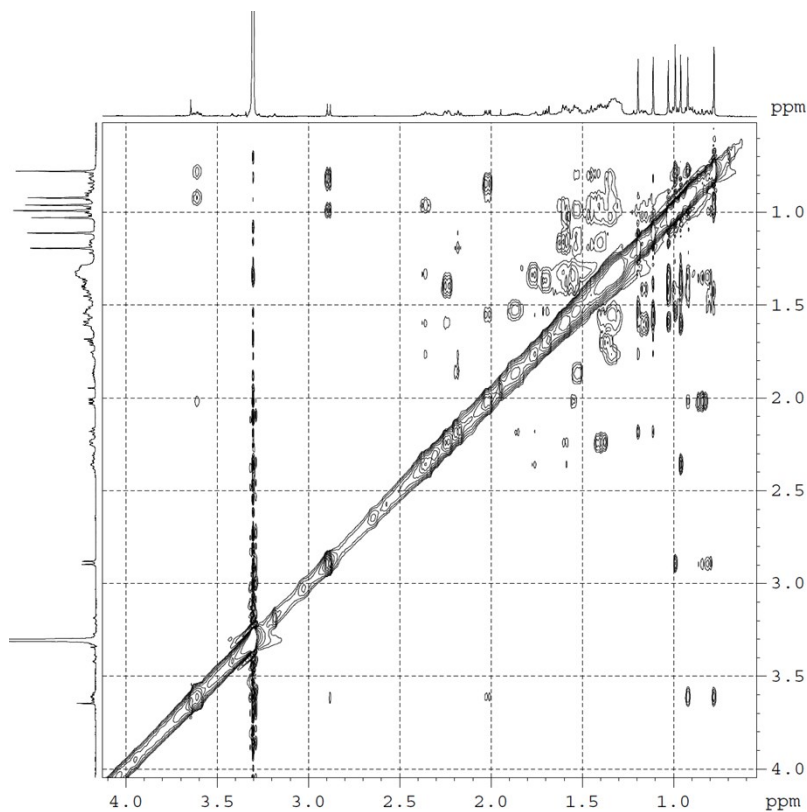
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FIDRES   517.384094 Hz
SW        213.382 ppm
FhMODE   QF

F2 - Processing parameters
SI        4096
SF        600.2000113 MHz
WDW       SINE
SSB       0
LB        0 Hz
GB        0
PC        1.40

F1 - Processing parameters
SI        1024
MC2       QF
SF        150.9202213 MHz
WDW       SINE
SSB       0
LB        0 Hz
GB        0
  
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Fig. S5. The HMBC (CD₃OD) spectrum of compound 1

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Current Data Parameters
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EXPNO    14
PROCNO   1

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PULPROG  noesypphpp
TD        2048
SOLVENT  MeOD
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DS        32
SWH       4629.39 Hz
FIDRES   4.521122 Hz
AQ        0.2211840 sec
RG        60.35
DW        108.000 usec
DE        10.00 usec
TE        303.0 K
DO        0.0009625 sec
D1        1.94920897 sec
D2        0.60000002 sec
D11       0.03000000 sec
D12       0.00002000 sec
D16       0.00020000 sec
INO       0.00021600 sec
TD0AV    1
SF01     600.2017038 MHz
NUC1      1H
P1        9.23 usec
P2        18.46 usec
P17      2500.00 usec
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GP21     40.00 %
P16      1000.00 usec

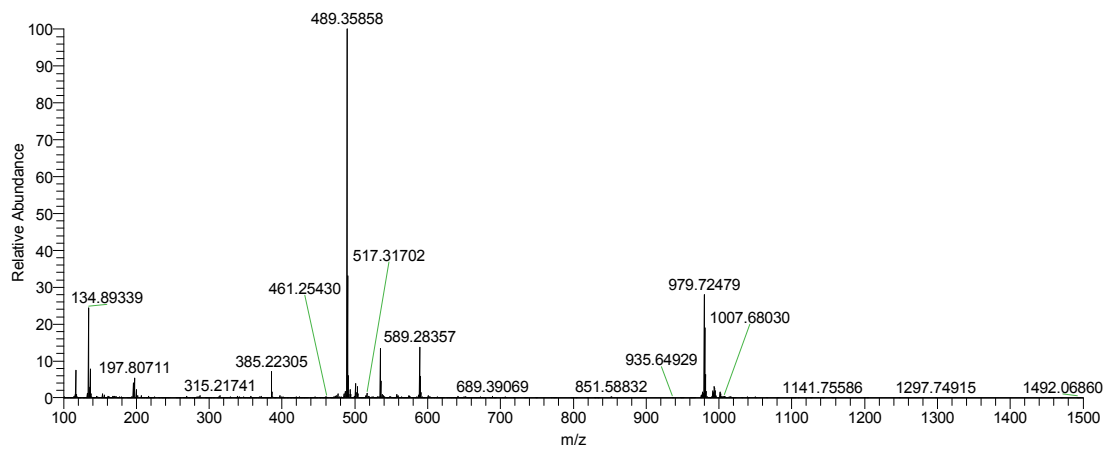
F1 - Acquisition parameters
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SW        7.713 ppm
FhMODE   States-TPPI

F2 - Processing parameters
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SF        600.2000130 MHz
WDW       QSINE
SSB       2
LB        0 Hz
GB        0
PC        1.00

F1 - Processing parameters
SI        1024
MC2       States-TPPI
SF        600.2000131 MHz
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SSB       2
LB        0 Hz
GB        0
  
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Fig. S6. The NOESY (CD₃OD) spectrum of compound 1

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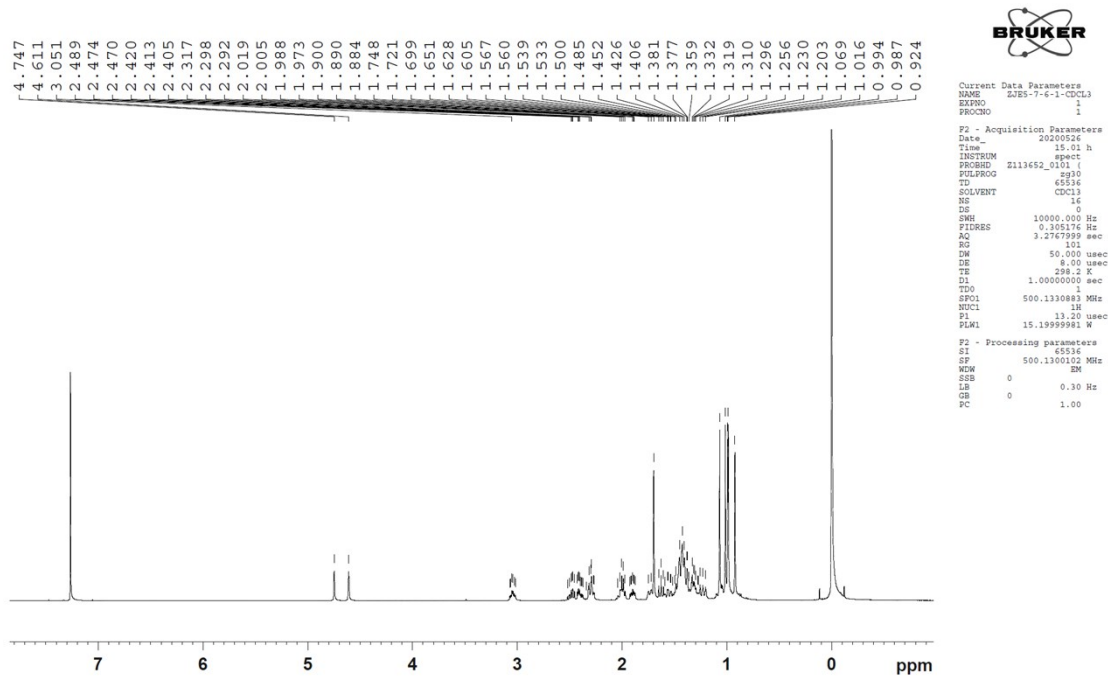


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Fig. S7. The ESI-Q-Orbitrap MS spectrum of compound **1**

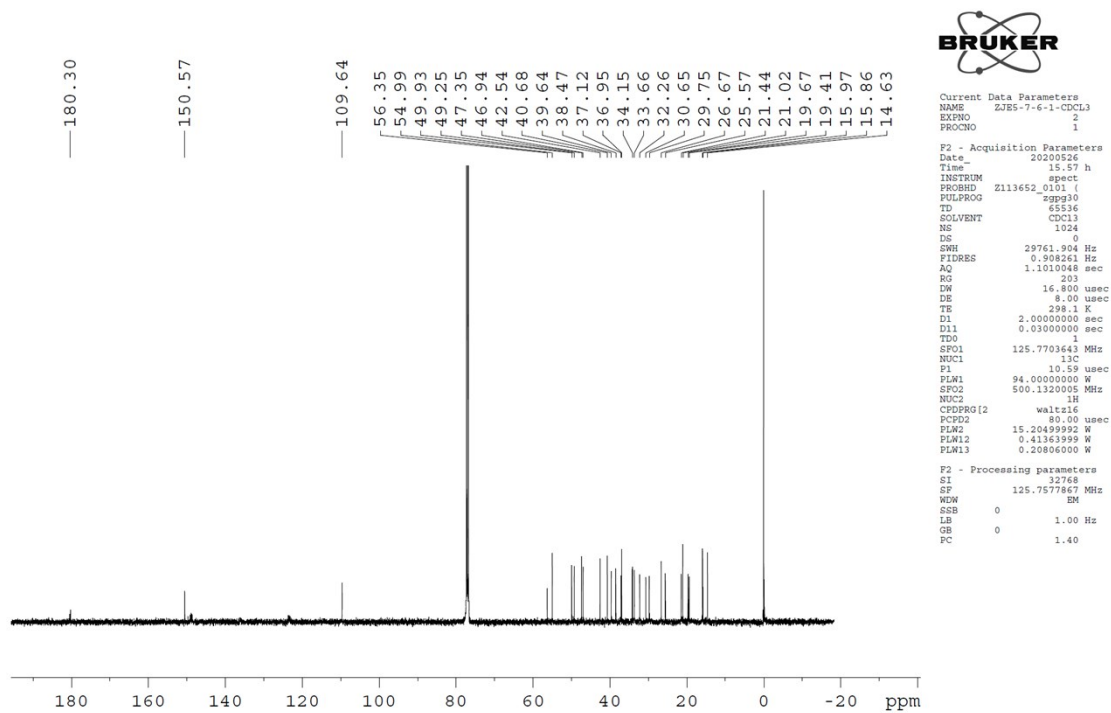
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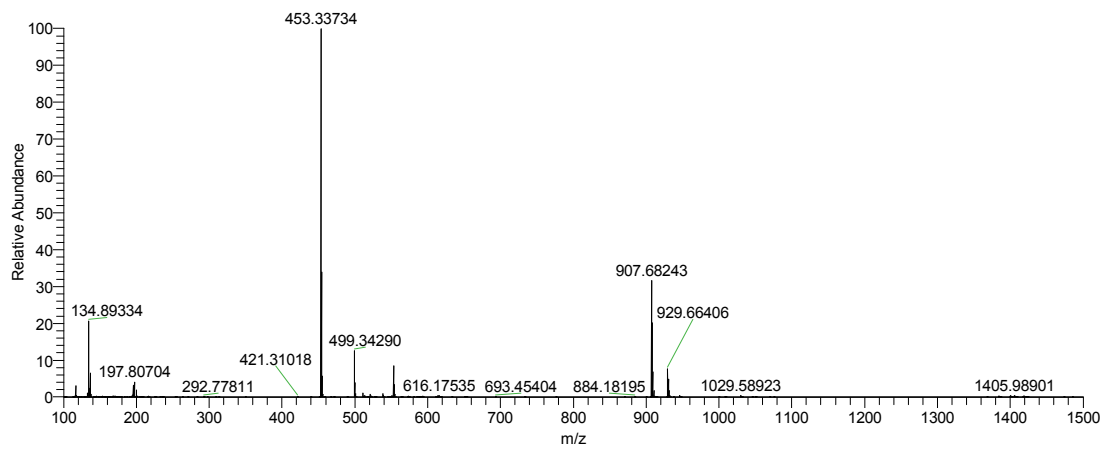
Fig. S8. ^1H NMR (500MHz, CDCl_3) spectrum of compound 2

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Fig. S9. ^{13}C NMR (125MHz, CDCl_3) spectrum of compound 2

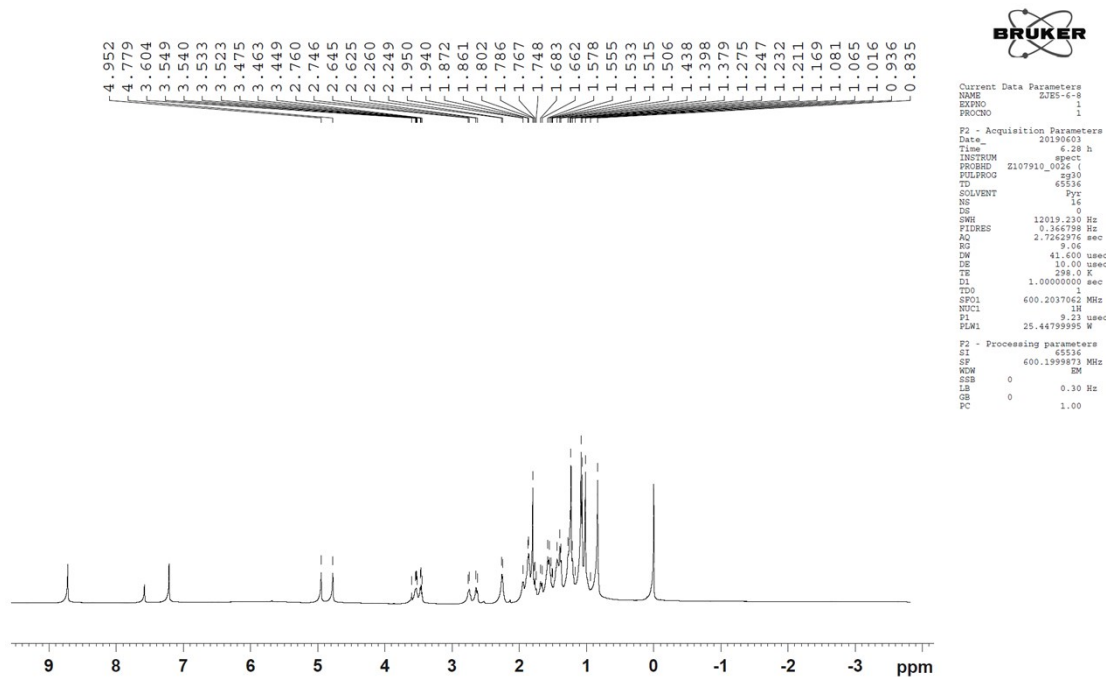


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Fig. S10. The ESI-Q-Orbitrap MS spectrum of compound **2**

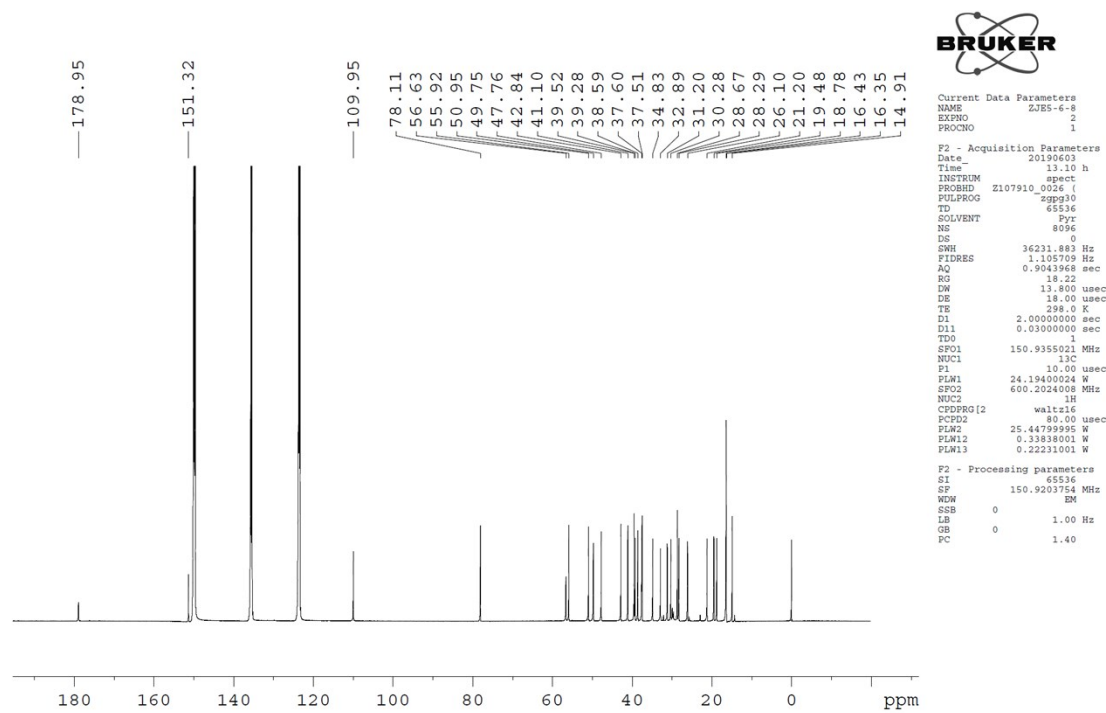
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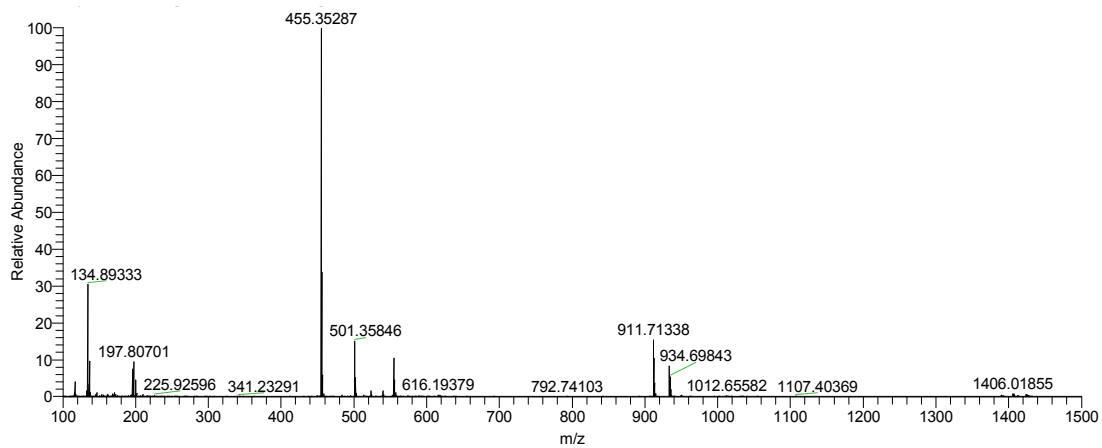
Fig. S11. ¹H NMR (600MHz, C₅D₅N) spectrum of compound 3

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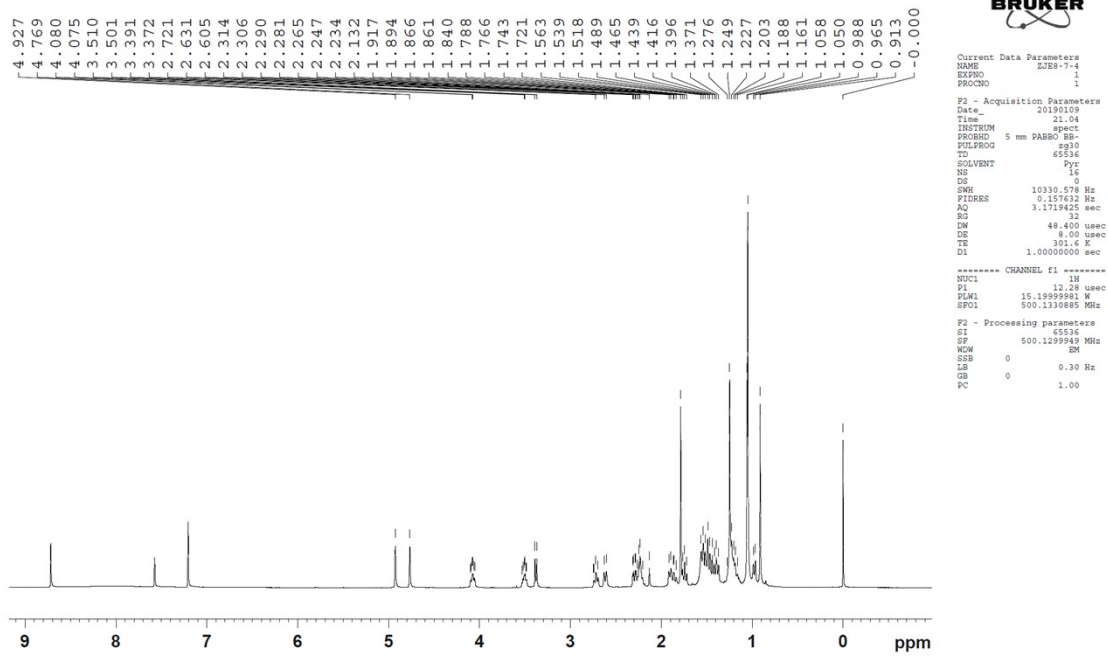
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Fig. S12. ¹³C NMR (150MHz, C₅D₅N) spectrum of compound 3

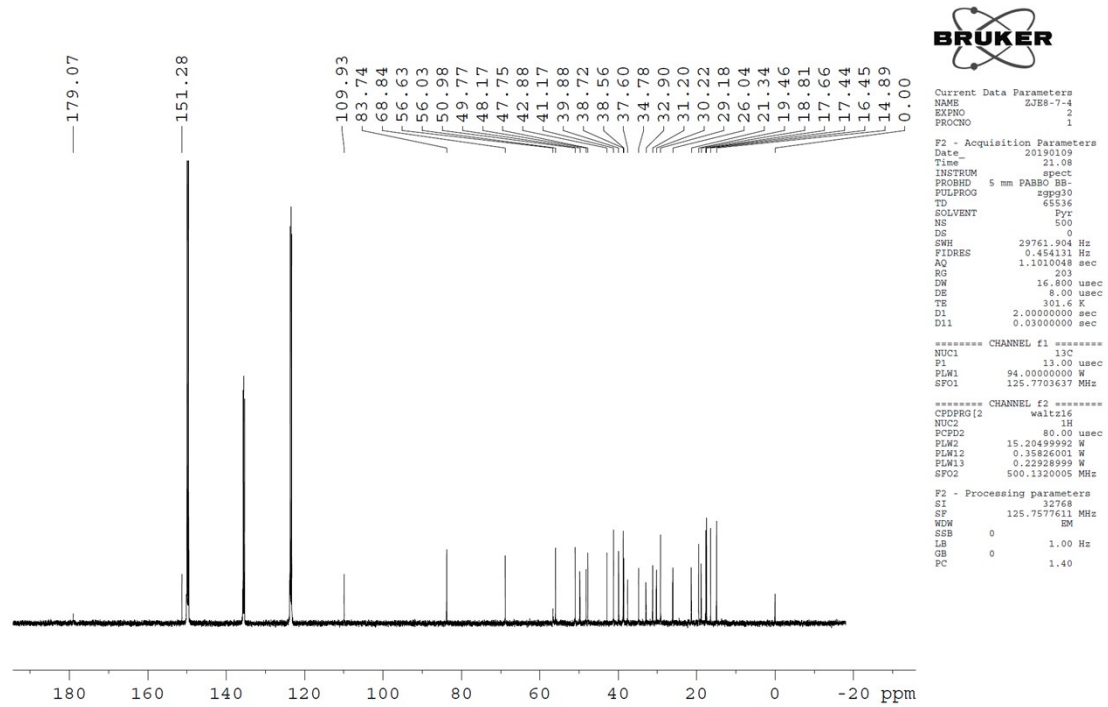


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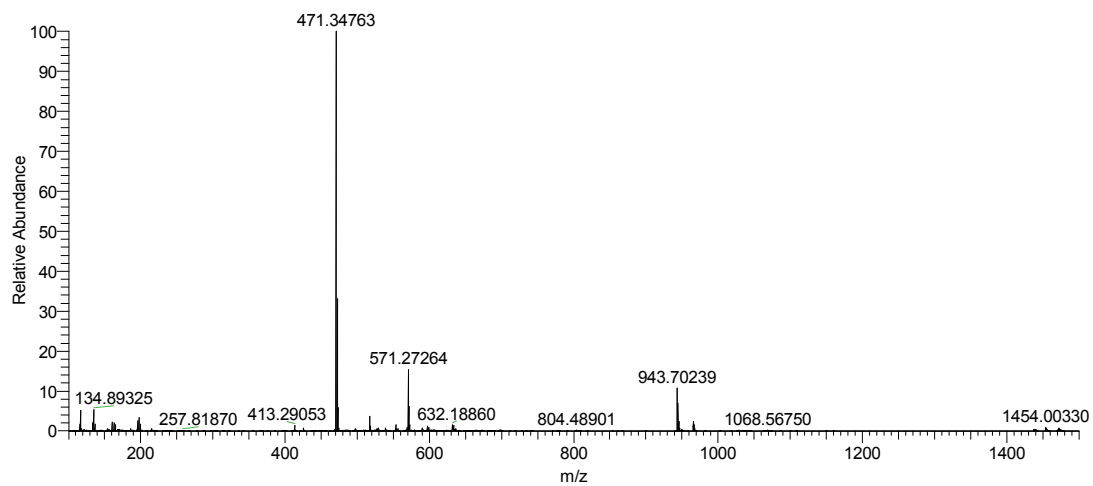
Fig. S13. The ESI-Q-Orbitrap MS spectrum of compound **3**



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Fig. S14. ^1H NMR (500MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum of compound 4

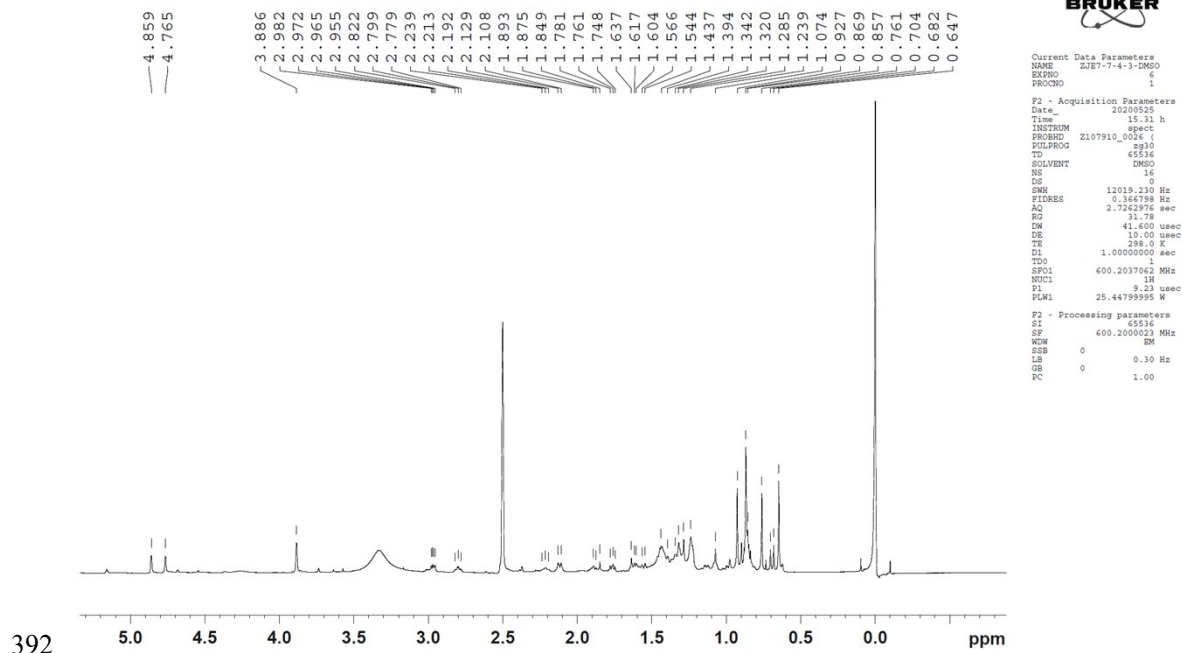


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Fig. S15. ^{13}C NMR (125MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum of compound 4



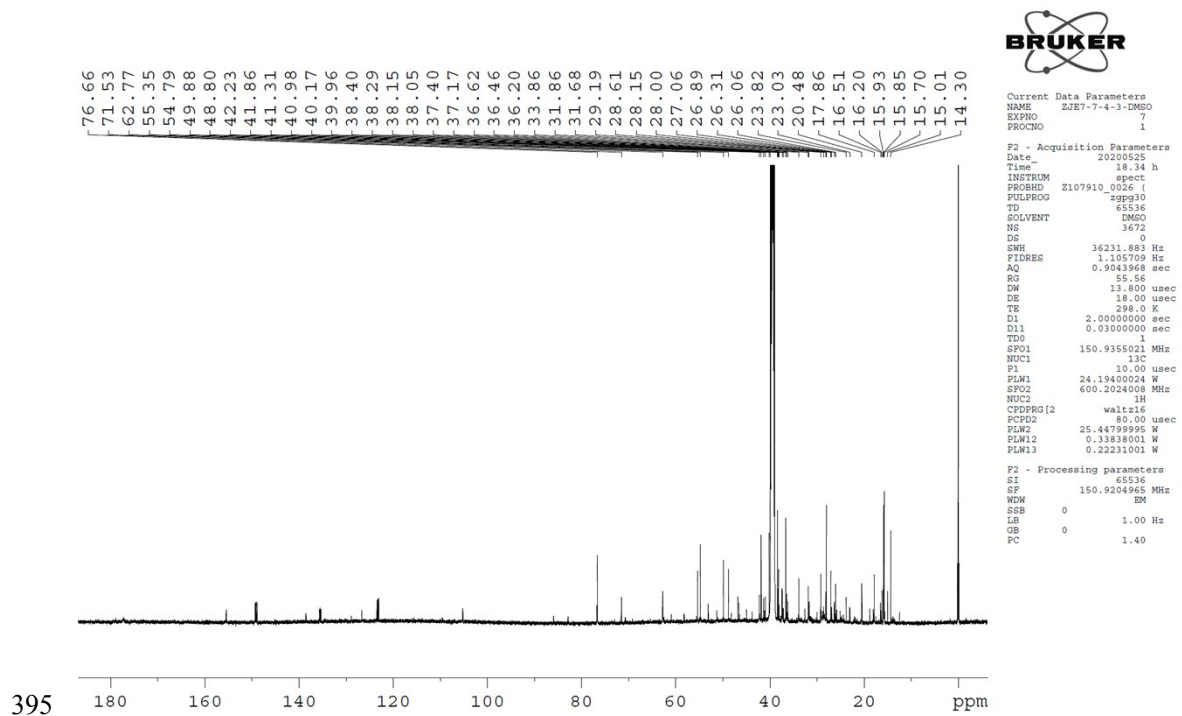
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Fig. S16. The ESI-Q-Orbitrap MS spectrum of compound **4**



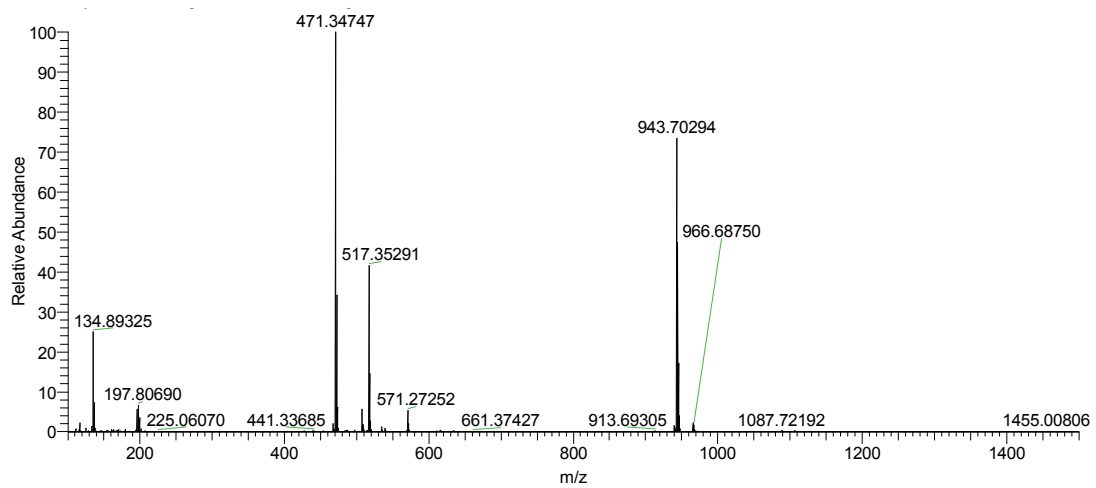
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Fig. S17. ¹H NMR (500MHz, C₅D₅N) spectrum of compound 5



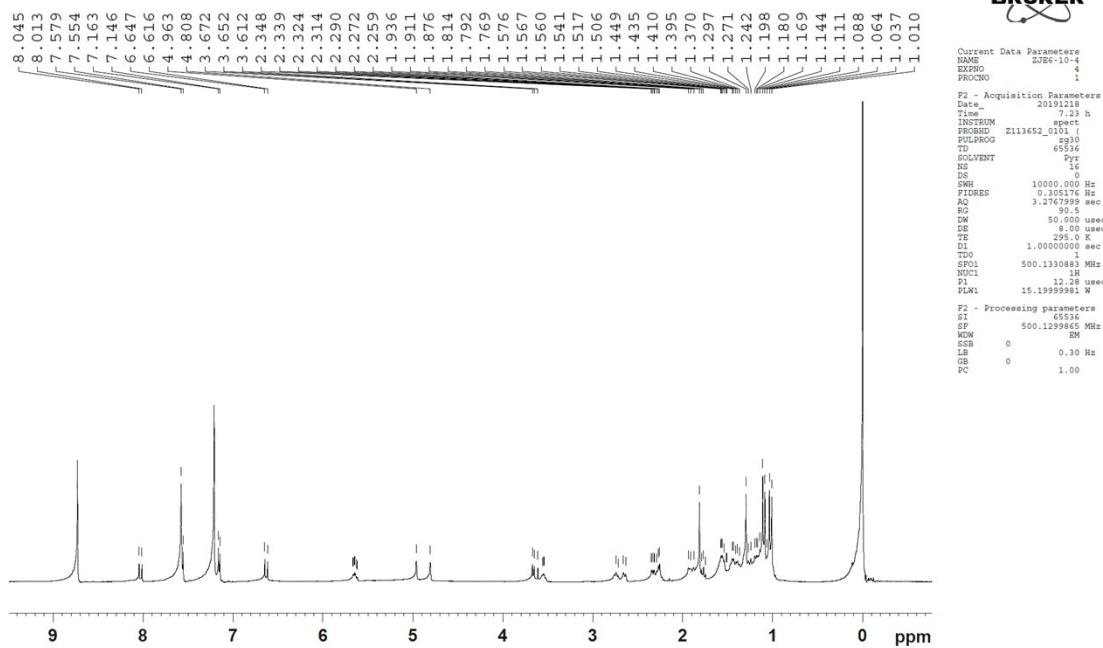
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Fig. S18. ¹³C NMR (125MHz, C₅D₅N) spectrum of compound 5



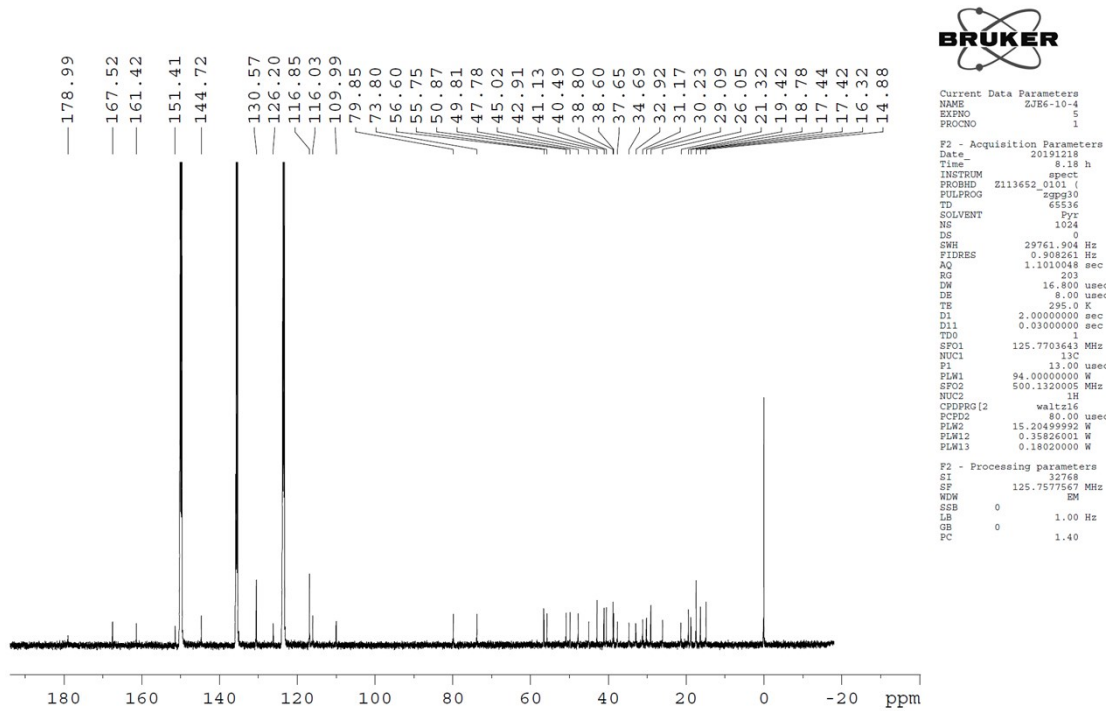
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401

Fig. S19. The ESI-Q-Orbitrap MS spectrum of compound **5**



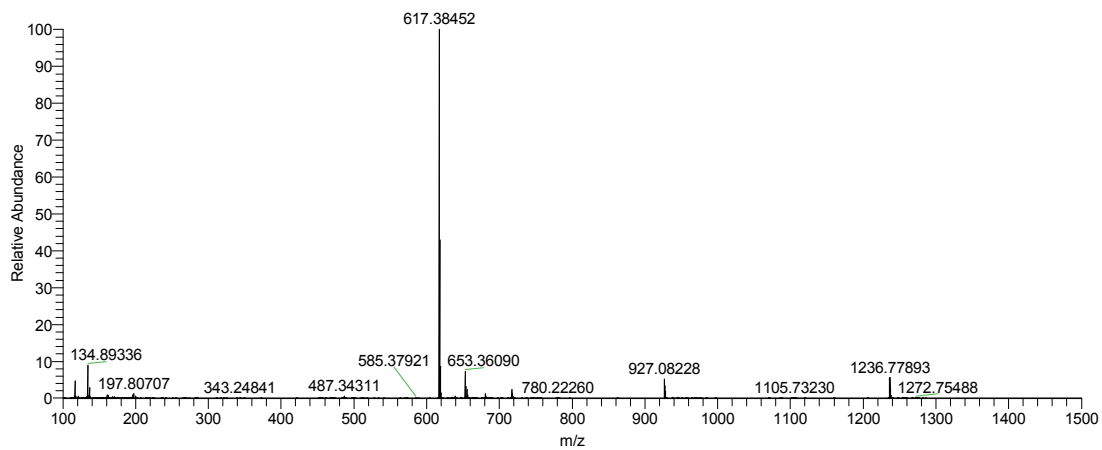
403
404
405

Fig. S20. ¹H NMR (500MHz, C₅D₅N) spectrum of compound 6



406
407
408

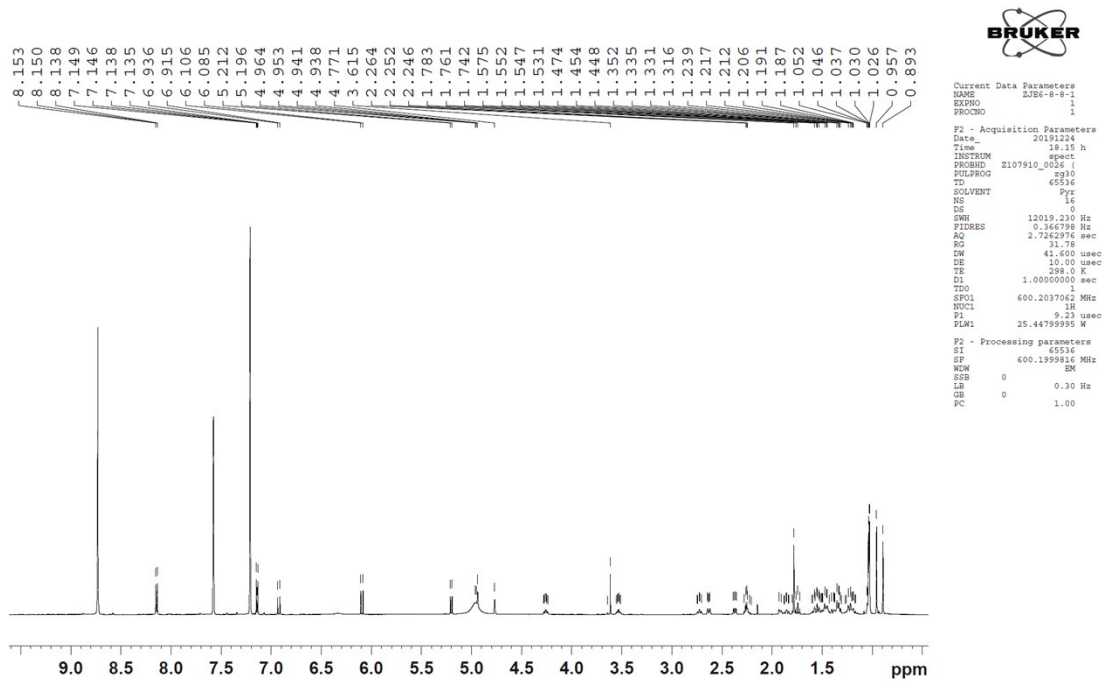
Fig. S21. ¹³C NMR (125MHz, C₅D₅N) spectrum of compound 6



409

410

Fig. S22. The ESI-Q-Orbitrap MS spectrum of compound **6**



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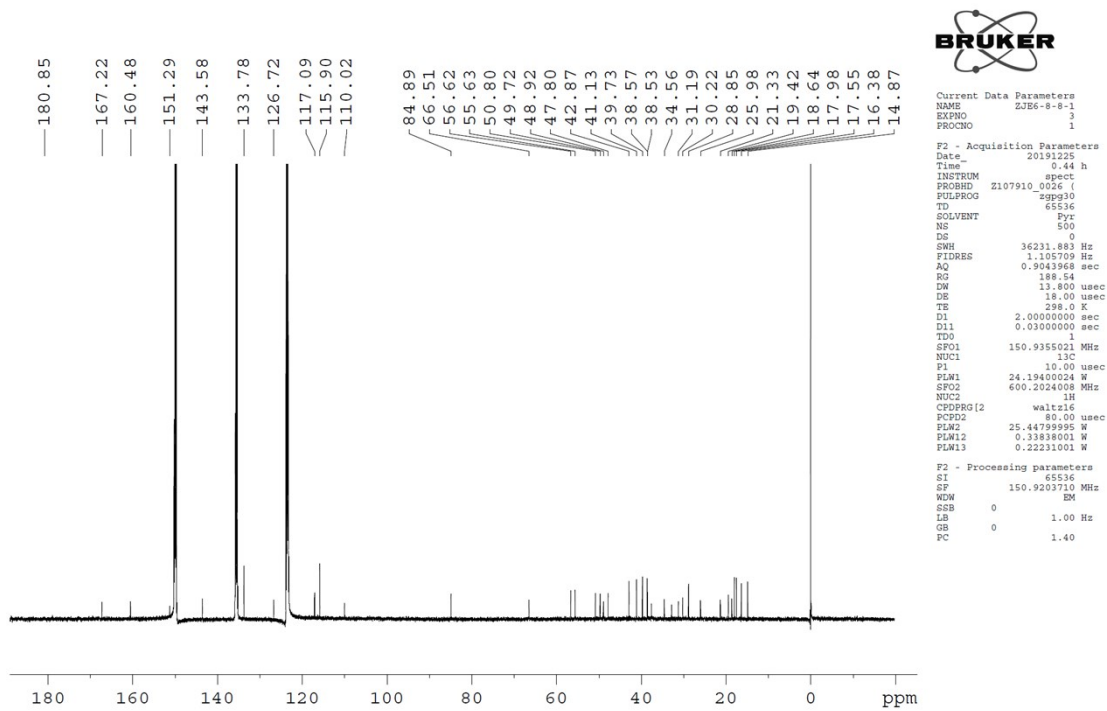
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EXPNO    1
PROCNO   1

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PULPROG  zg30
TD        65536
SOLVENT  Pyr
NS        0
DS        0
SWH       12019.230 Hz
FIDRES    0.366798 Hz
AQ        2.7262976 sec
RG        31.78
DW        41.600 usec
DE        10.00 usec
TE        298.0 K
D1        1.00000000 sec
TDO       1
SFO1      600.2037062 MHz
NUC1      1H
D11       9.23 usec
PLW1      25.44798995 W

F2 - Processing parameters
SI        65536
SF        600.1999816 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
  
```

412
413
414

Fig. S23. ^1H NMR (600MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum of compound 7



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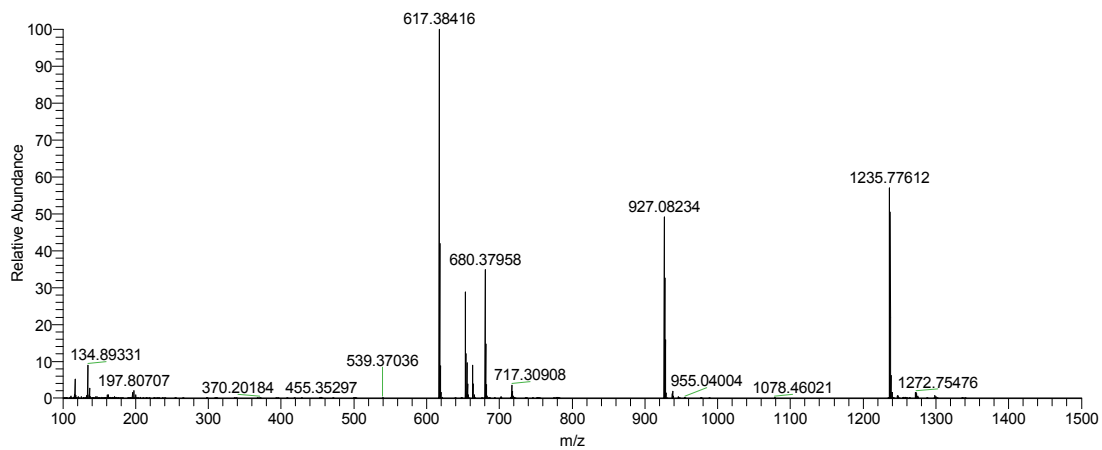
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EXPNO    3
PROCNO   1

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Time     0.44 h
INSTRUM  spect
PROBHD   zgpg30
PULPROG  zg30
TD        65536
SOLVENT  Pyr
NS        500
DS        0
SWH       36231.883 Hz
FIDRES    1.105709 Hz
AQ        0.2943868 sec
RG        188.54
DW        13.800 usec
DE        18.00 usec
TE        298.0 K
D1        2.00000000 sec
D11       0.03000000 sec
TDO       1
SFO1      150.9355021 MHz
NUC1      13C
D11       10.00 usec
PLW1      24.19400024 W
SFO2      600.2024008 MHz
NUC2      1H
CPDPRG2  waltz16
PCPD2    80.00 usec
PLW2     25.44798995 W
PLW12    0.33838001 W
PLW13    0.22231001 W

F2 - Processing parameters
SI        65536
SF        150.9203710 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
  
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415
416
417

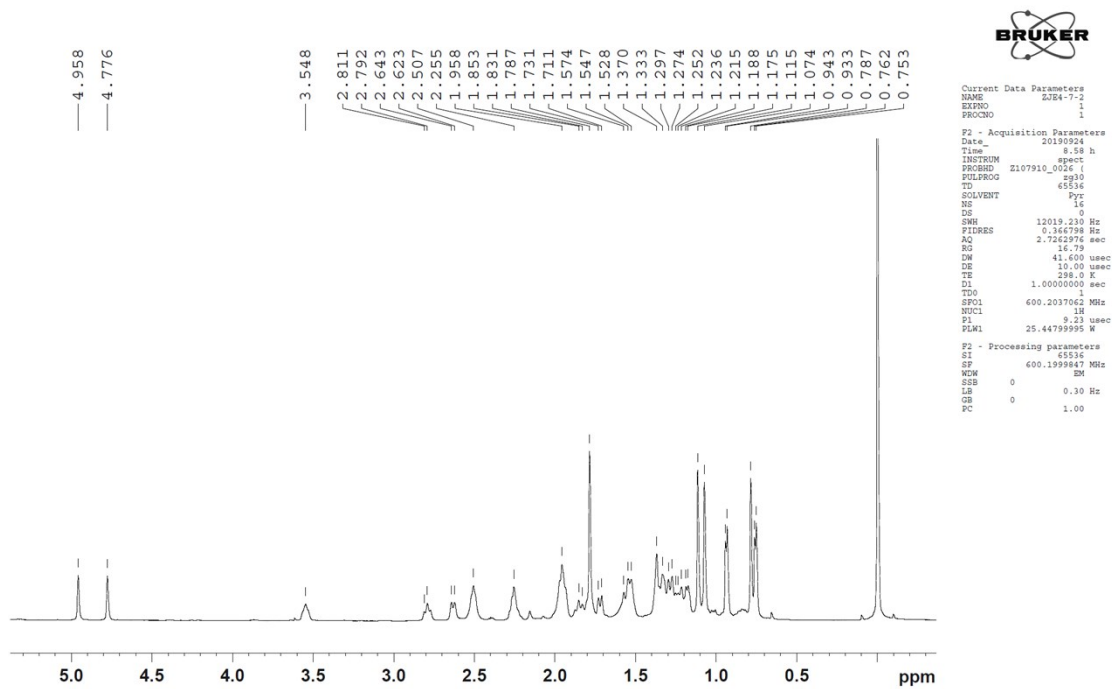
Fig. S24. ^{13}C NMR (150MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum of compound 7



418

419

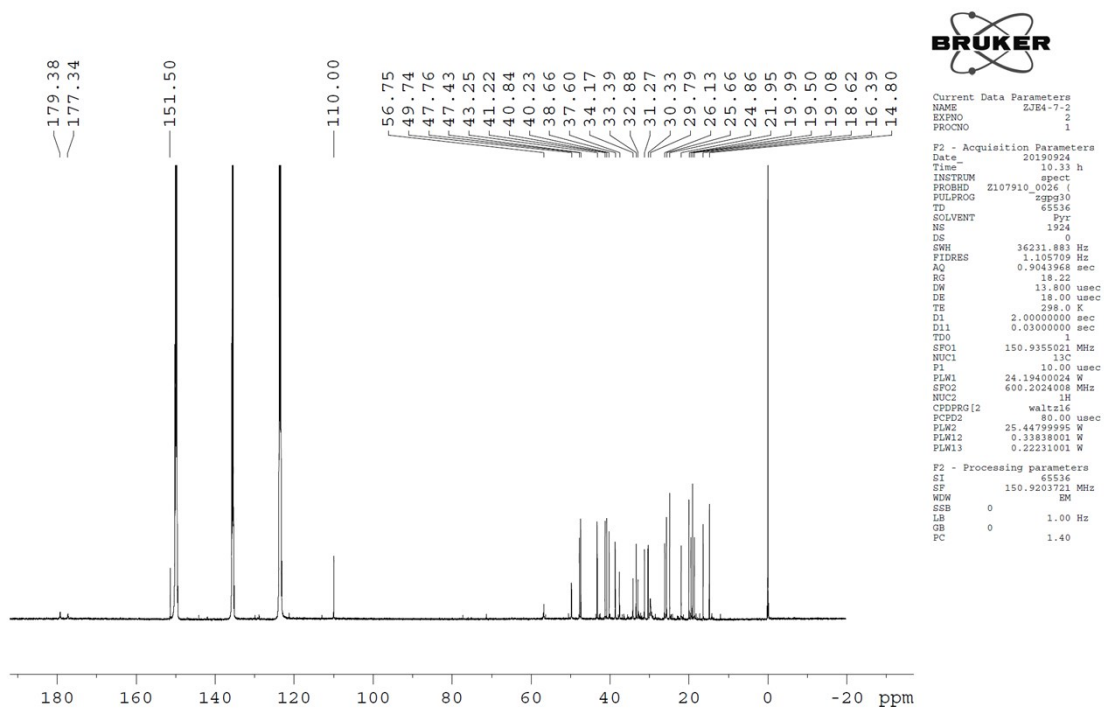
Fig. S25. The ESI-Q-Orbitrap MS spectrum of compound 7



422

423

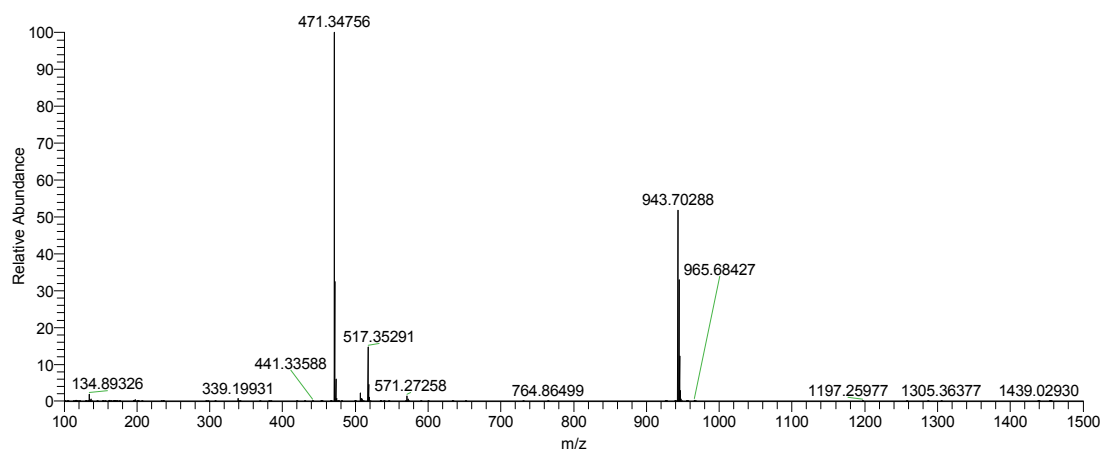
424

Fig. S26. ^1H NMR (600MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum of compound 8

425

426

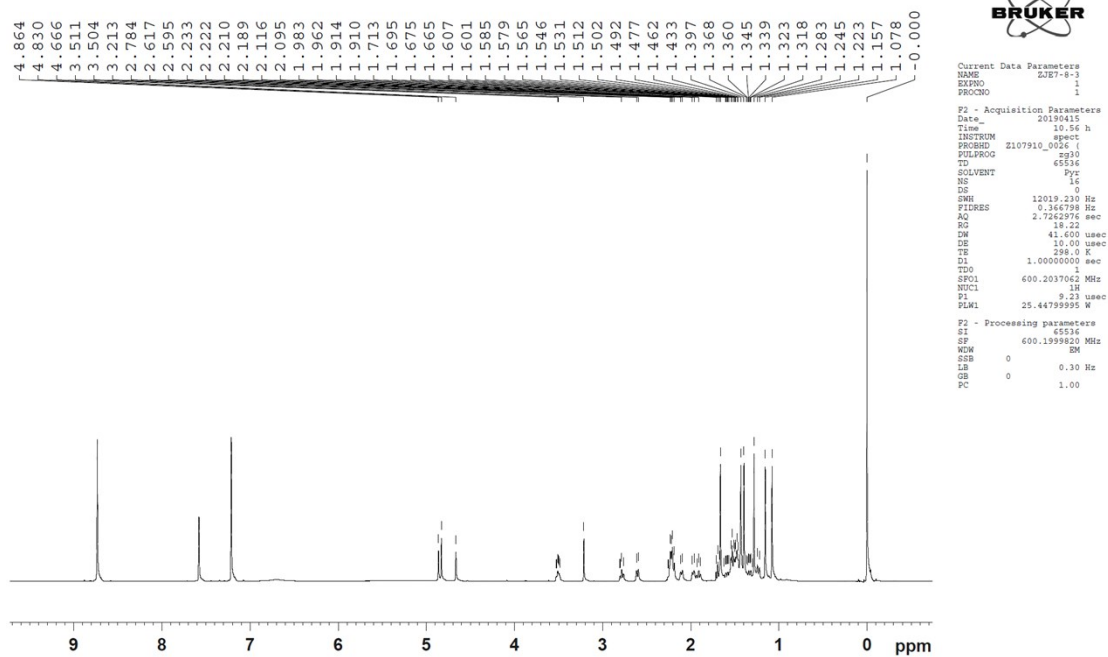
Fig. S27. ^{13}C NMR (150MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum of compound 8



428

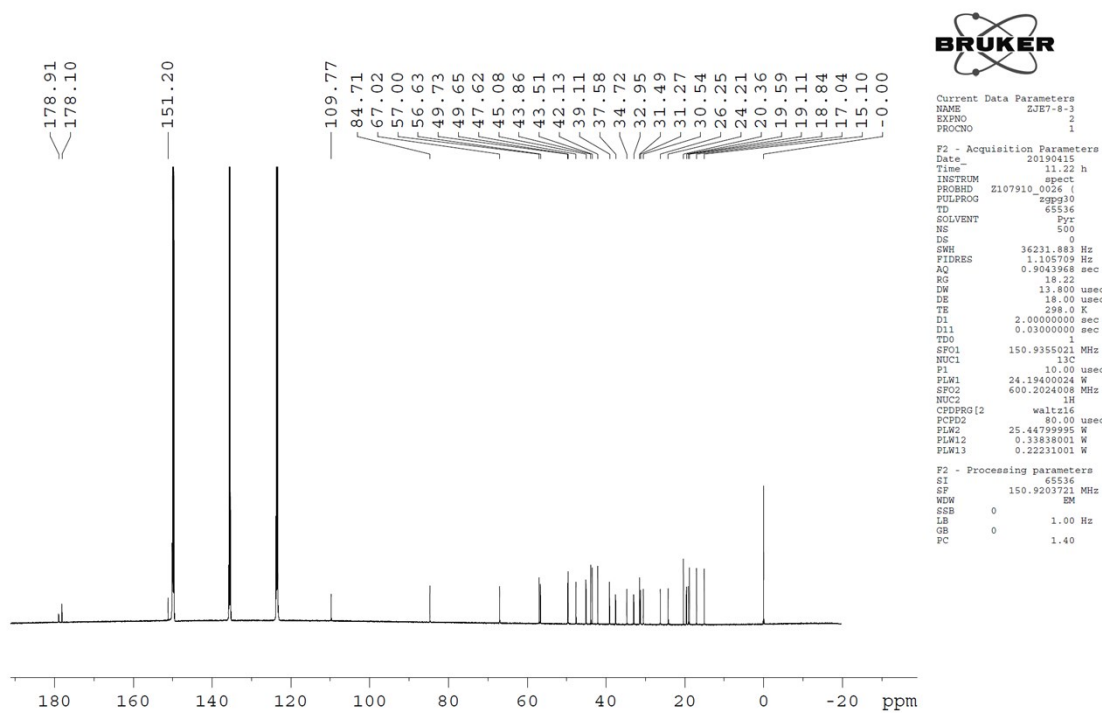
429

Fig. S28. The ESI-Q-Orbitrap MS spectrum of compound **8**



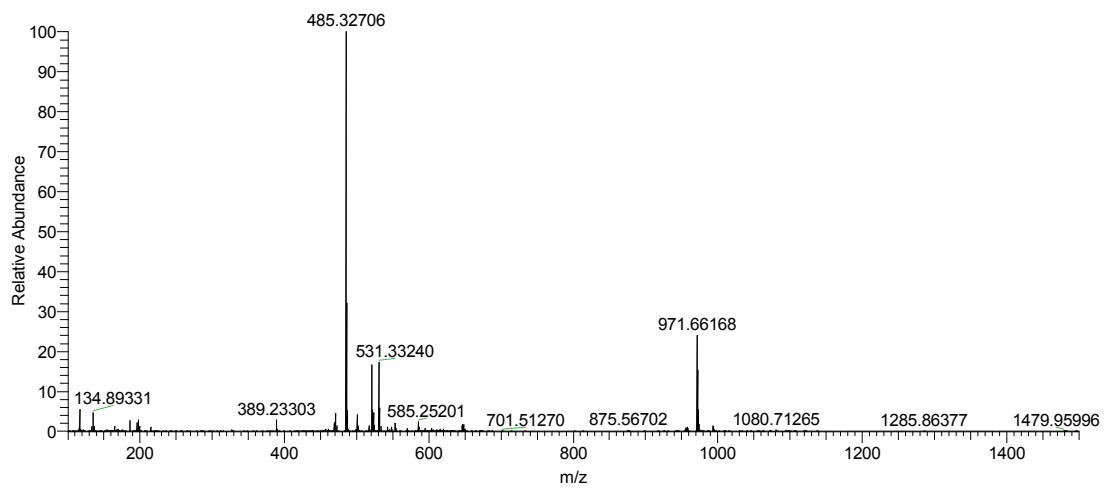
431
432
433

Fig. S29. ¹H NMR (600MHz, C₅D₅N) spectrum of compound 9



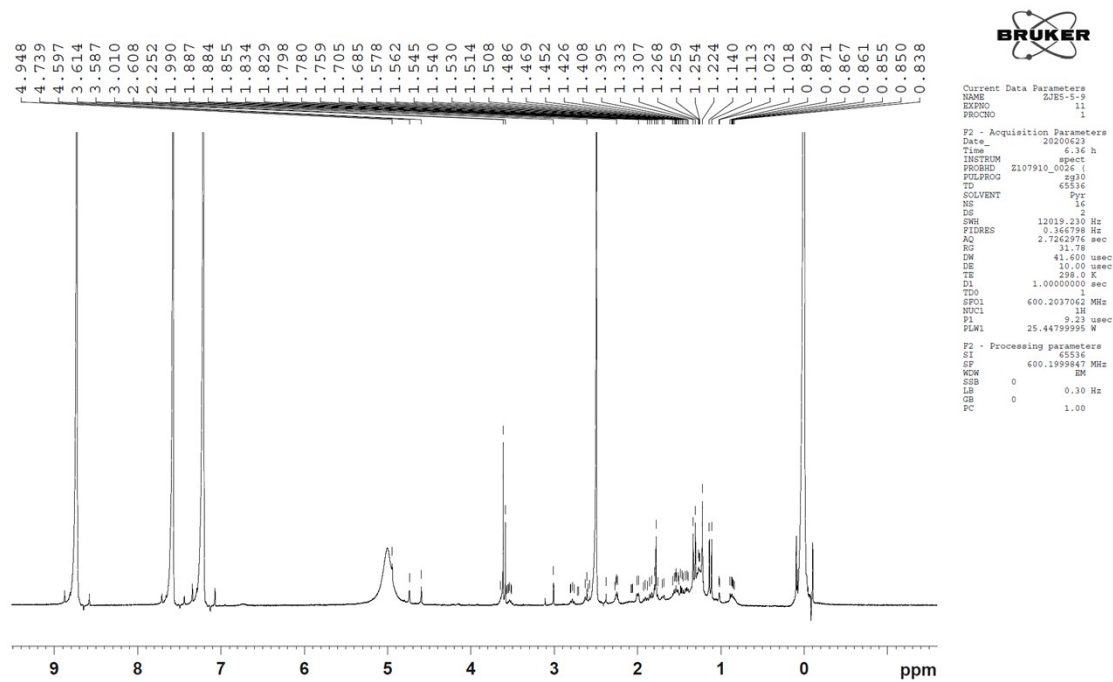
434
435
436

Fig. S30. ¹³C NMR (150MHz, C₅D₅N) spectrum of compound 9



437
438
439

Fig. S31. The ESI-Q-Orbitrap MS spectrum of compound **9**



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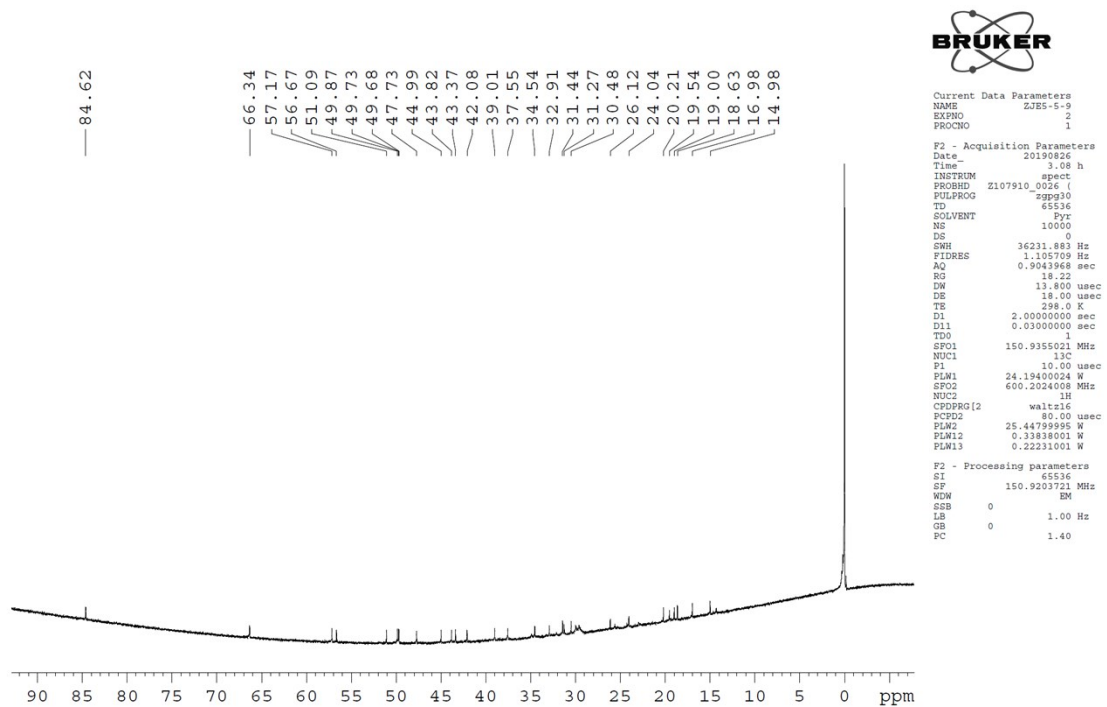
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EXPNO    1
PROCNO   1

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PROBHD   Z107910_0025 (
PULPROG  zgpg30
TD        65536
SOLVENT  Pyr
NS        16
DS        2
SWH       12019.230 Hz
FIDRES    0.366798 Hz
AQ        2.7262976 sec
RG        31.78
DM        41.600 usec
DE        10.00 usec
TE        298.0 K
D1        1.00000000 sec
TDO       0
SFO1      600.2037062 MHz
NUC1      1H
P1        9.23 usec
PLM1      25.44799995 W

F2 - Processing parameters
SI        65536
SF        600.1999847 MHz
WDW       EM
SSB       0
LB        0.10 Hz
GB        0
PC        1.00
  
```

441
442
443

Fig. S32. ¹H NMR (600MHz, C₅D₅N) spectrum of compound 10



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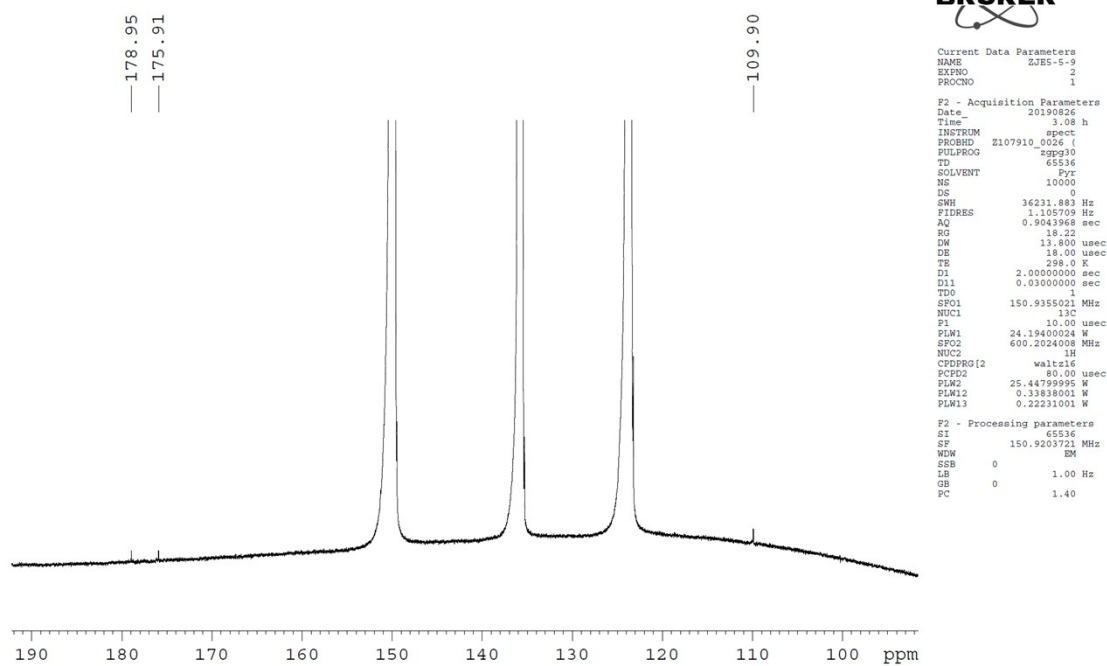
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EXPNO    2
PROCNO   1

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INSTRUM  spect
PROBHD   Z107910_0026 (
PULPROG  zgpg30
TD        65536
SOLVENT  Pyr
NS        10000
DS        0
SWH       36231.883 Hz
FIDRES    1.105709 Hz
AQ        0.9043988 sec
RG        18.22
DM        13.800 usec
DE        18.00 usec
TE        298.0 K
D1        2.00000000 sec
D11       0.03000000 sec
TDO       1
SFO1      150.9355021 MHz
NUC1      13C
P1        10.00 usec
PLM1      24.19400024 W
SFO2      600.2024008 MHz
NUC2      1H
CPDPRG2  waltz16
PCPD2     80.00 usec
PLM2      25.44799995 W
PLM12     0.33838001 W
PLM13     0.22331001 W

F2 - Processing parameters
SI        65536
SF        150.9203721 MHz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
  
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444
445
446

Fig. S33. ¹³C NMR (150MHz, C₅D₅N) spectrum-1 of compound 10

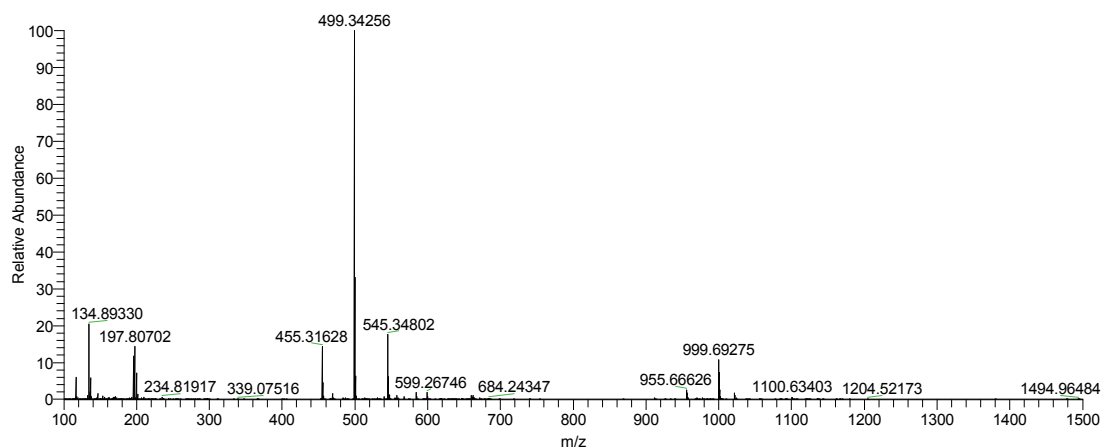


447

Fig. S34. ^{13}C NMR (150MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum-2 of compound **10**

448

449

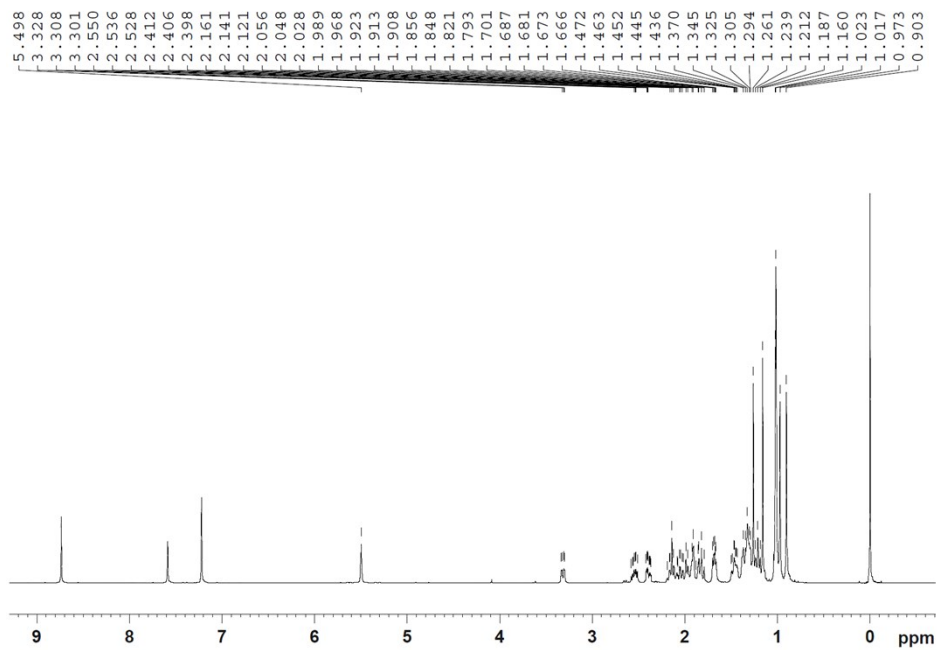


450

Fig. S35. The ESI-Q-Orbitrap MS spectrum of compound **10**

451

452



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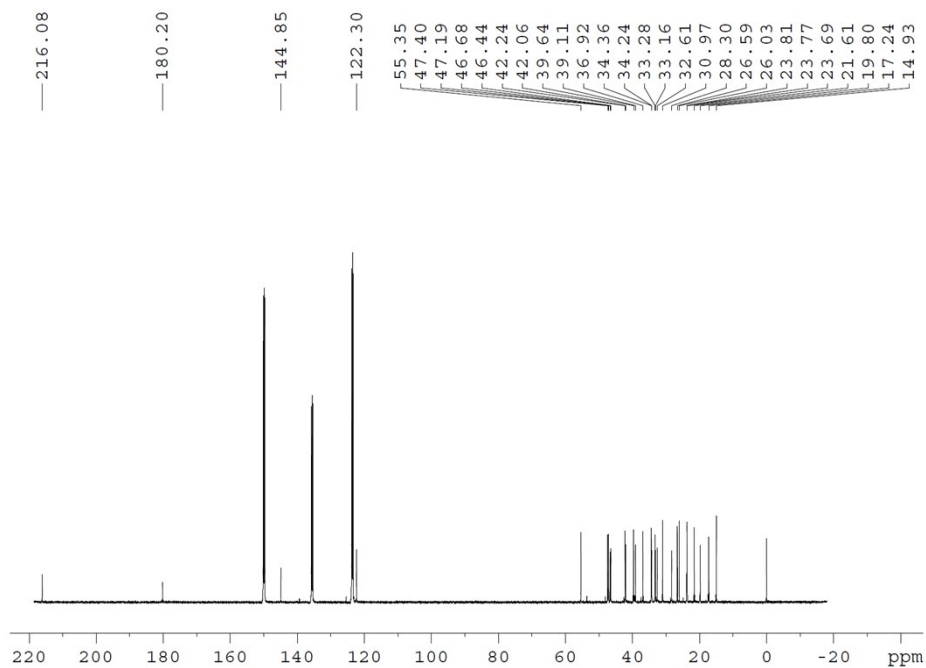
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 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20191217
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 PULPROG zgpg30
 TD 65536
 SOLVENT Pyr
 NS 16
 DS 0
 SWH 10000.000 Hz
 FIDRES 0.105176 Hz
 AQ 3.2767999 sec
 RG 32
 DW 50.000 usec
 DE 8.00 usec
 TE 295.3 K
 TI 1.0000000 sec
 TDO 1
 SFO1 500.1310083 MHz
 NUC1 1H
 PL 32.28 usec
 PLW1 15.19999981 W

F2 - Processing parameters
 SI 65536
 SF 500.1299998 MHz
 WDN 0 EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

454
455
456

Fig. S36. ¹H NMR (500MHz, C₅D₅N) spectrum of compound 11



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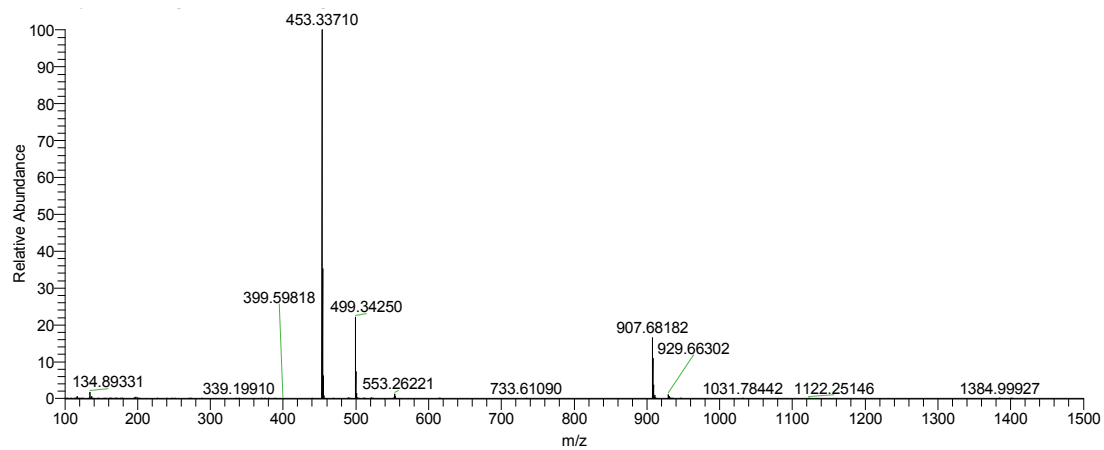
Current Data Parameters
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 EXPNO 3
 PROCNO 1

F2 - Acquisition Parameters
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 Time 23.24 h
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 PULPROG zgpg30
 TD 65536
 SOLVENT Pyr
 NS 512
 DS 0
 SWH 29761.904 Hz
 FIDRES 0.908261 Hz
 AQ 1.1010048 sec
 RG 203
 DW 16.800 usec
 DE 8.00 usec
 TE 295.0 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TDO 1
 SFO1 125.7703641 MHz
 NUC1 13C
 PL 13.00 usec
 PLW1 94.0000000 W
 SFO2 500.1320005 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 80.00 usec
 PLW2 15.20499992 W
 PLW12 0.35826001 W
 PLW13 0.18020000 W

F2 - Processing parameters
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 SF 125.7577594 MHz
 WDN 0 EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

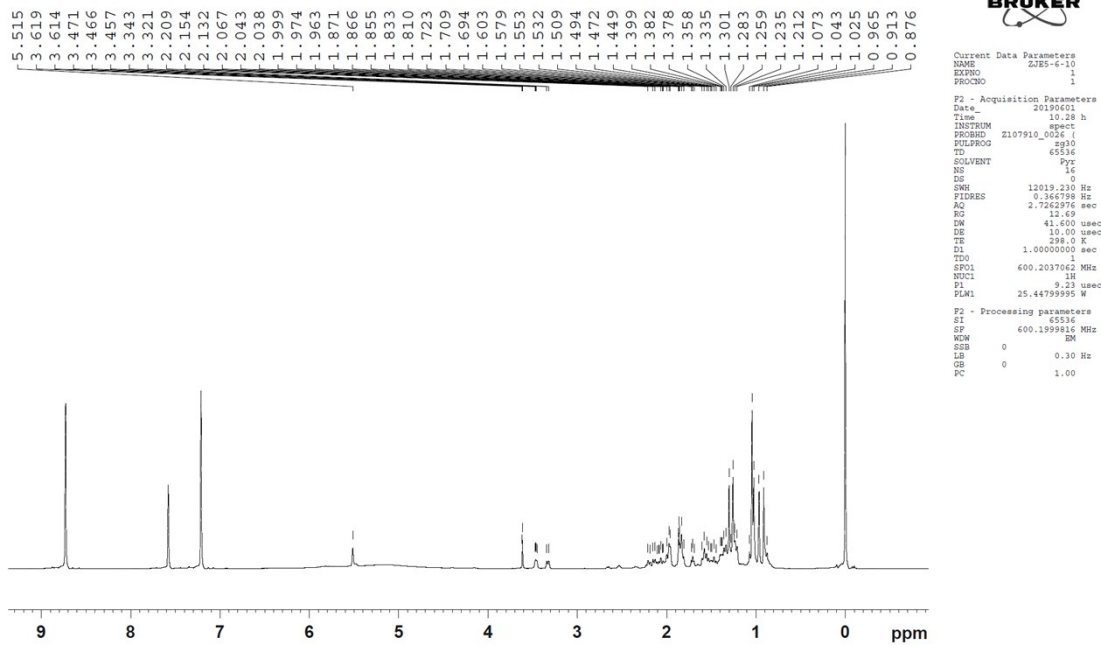
457
458
459

Fig. S37. ¹³C NMR (125MHz, C₅D₅N) spectrum of compound 11



460
461
462

Fig. S38. The ESI-Q-Orbitrap MS spectrum of compound **11**

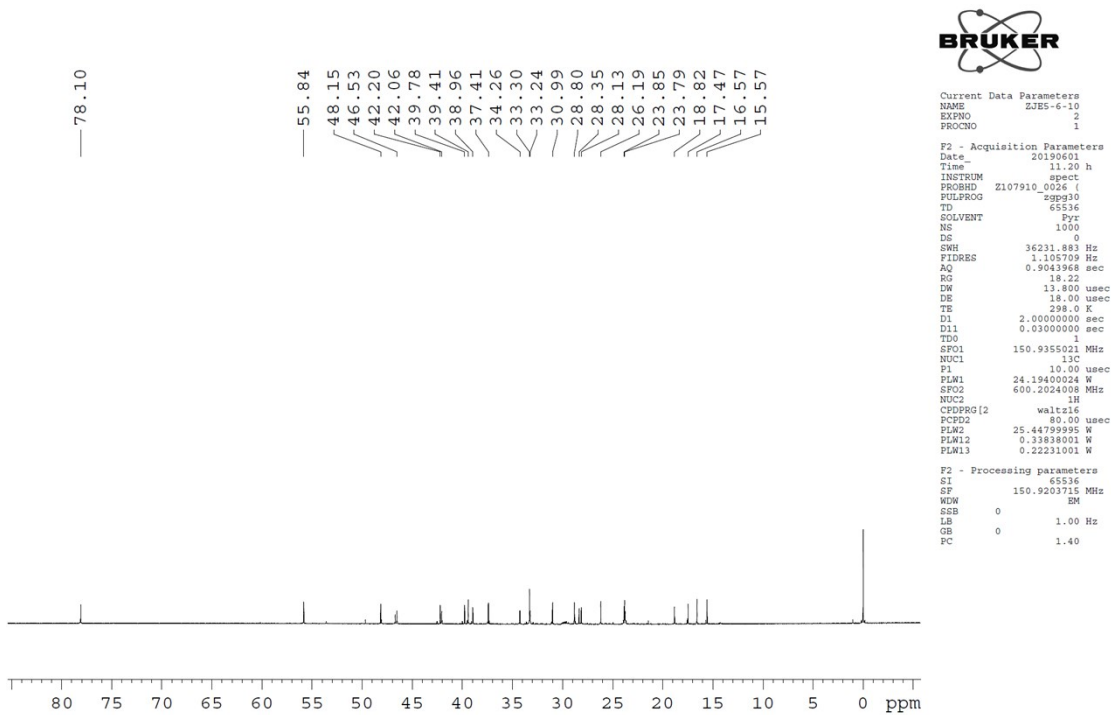


464

465

466

Fig. S39. ^1H NMR (600MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum of compound 12

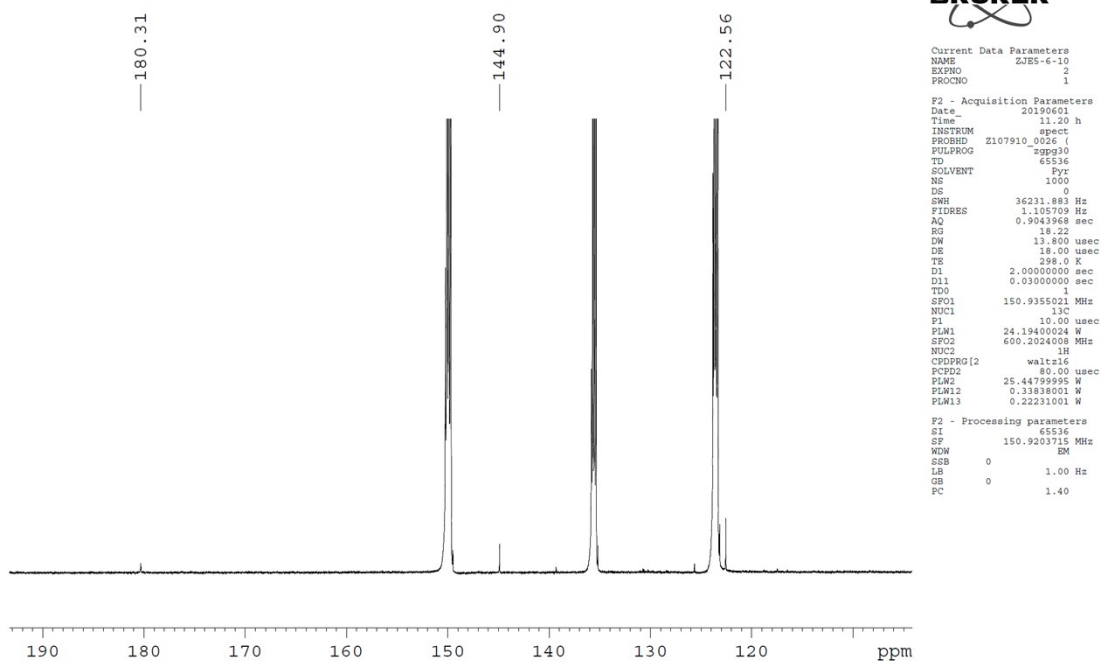


467

468

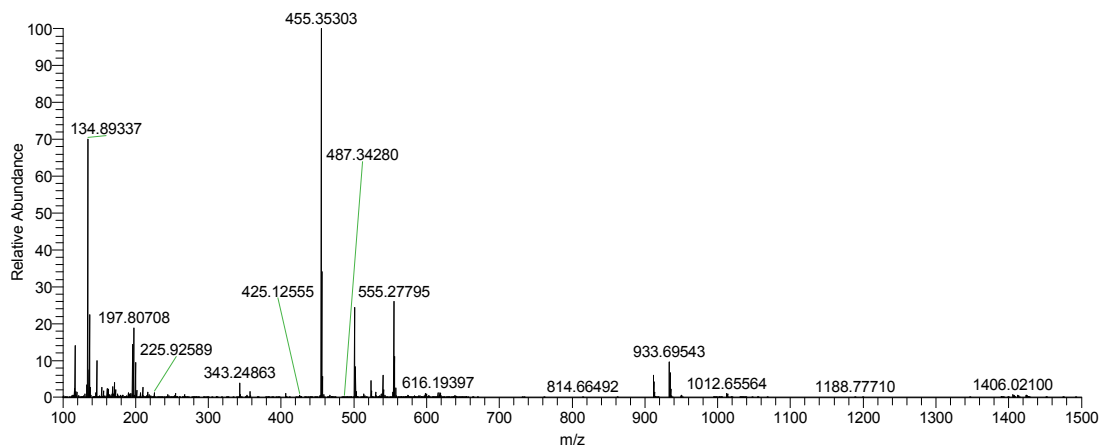
469

Fig. S40. ^{13}C NMR (150MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum-1 of compound 12



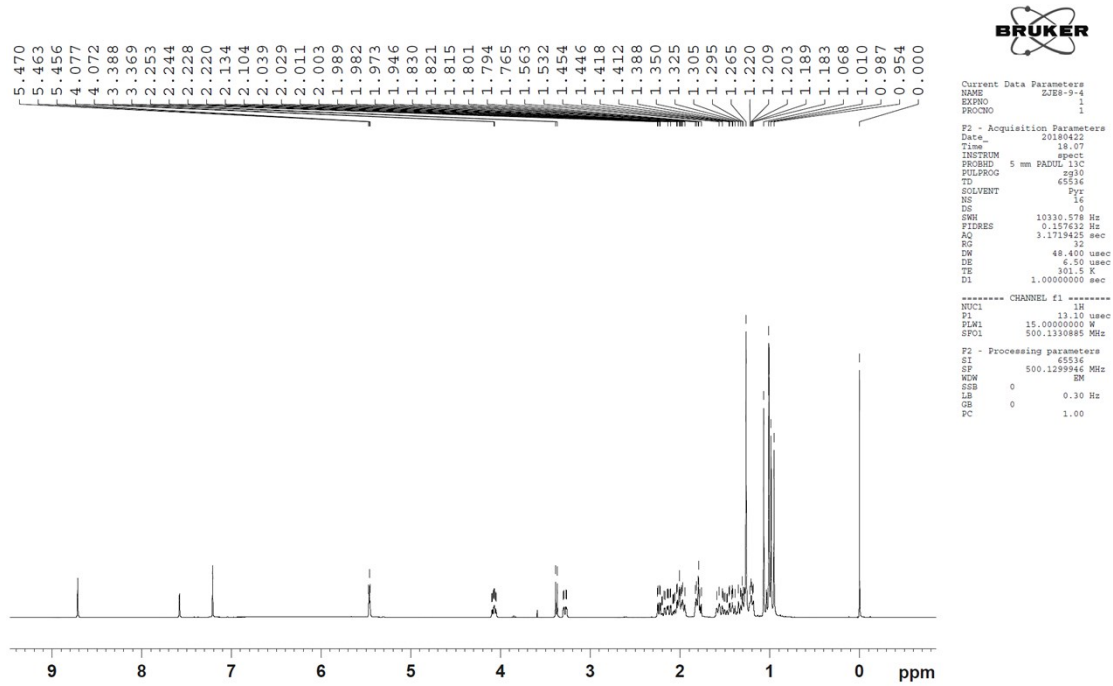
470
471
472

Fig. S41. ¹³C NMR (150MHz, C₅D₅N) spectrum-2 of compound 12



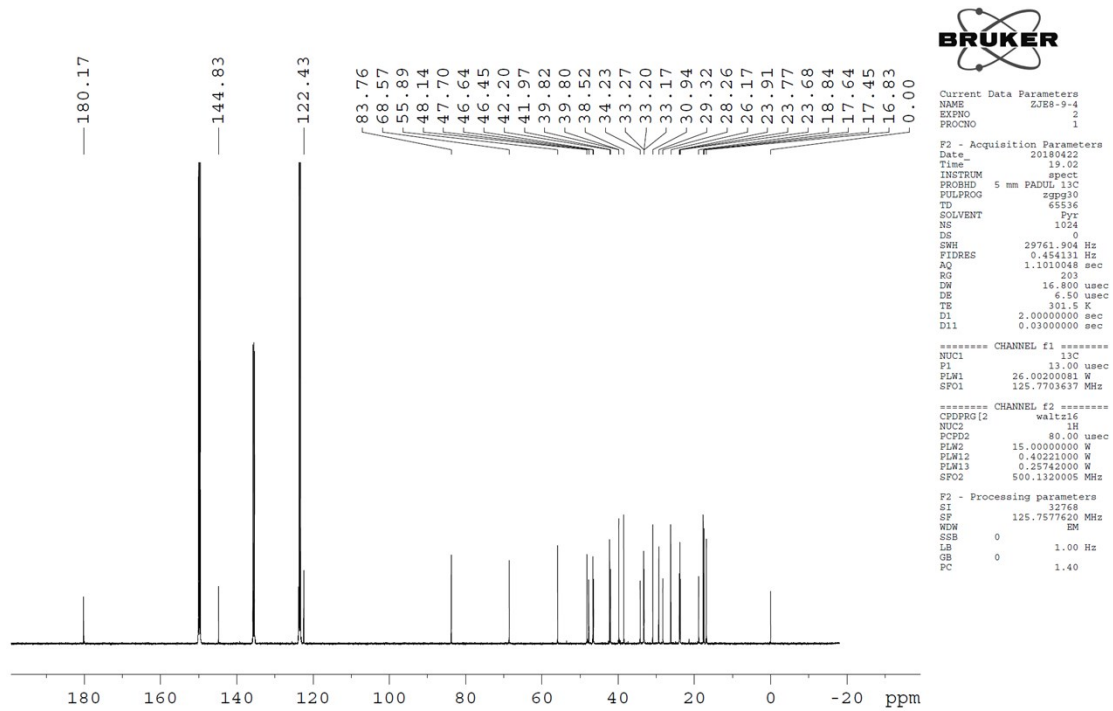
473
474
475

Fig. S42. The ESI-Q-Orbitrap MS spectrum of compound 12



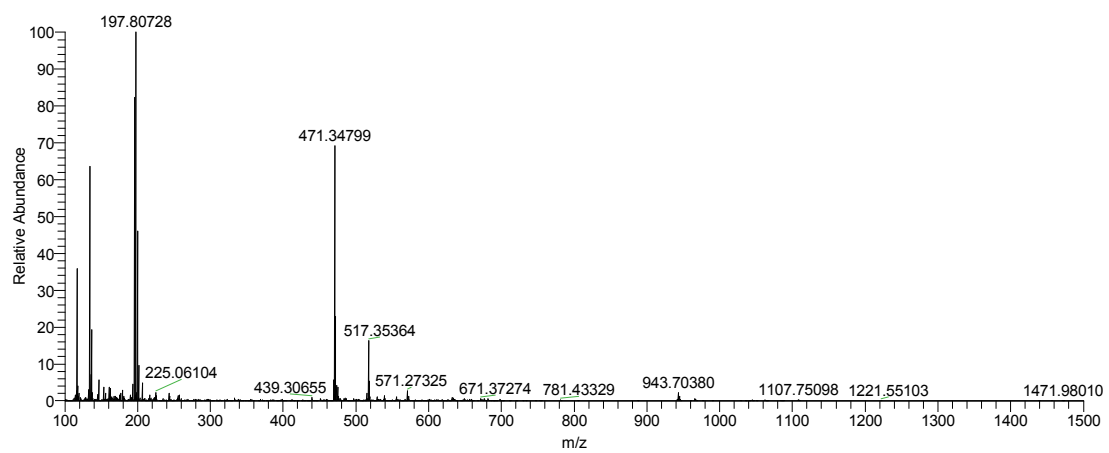
477
478
479

Fig. S43. ¹H NMR (500MHz, C₅D₅N) spectrum of compound 13



480
481
482

Fig. S44. ¹³C NMR (125MHz, C₅D₅N) spectrum of compound 13

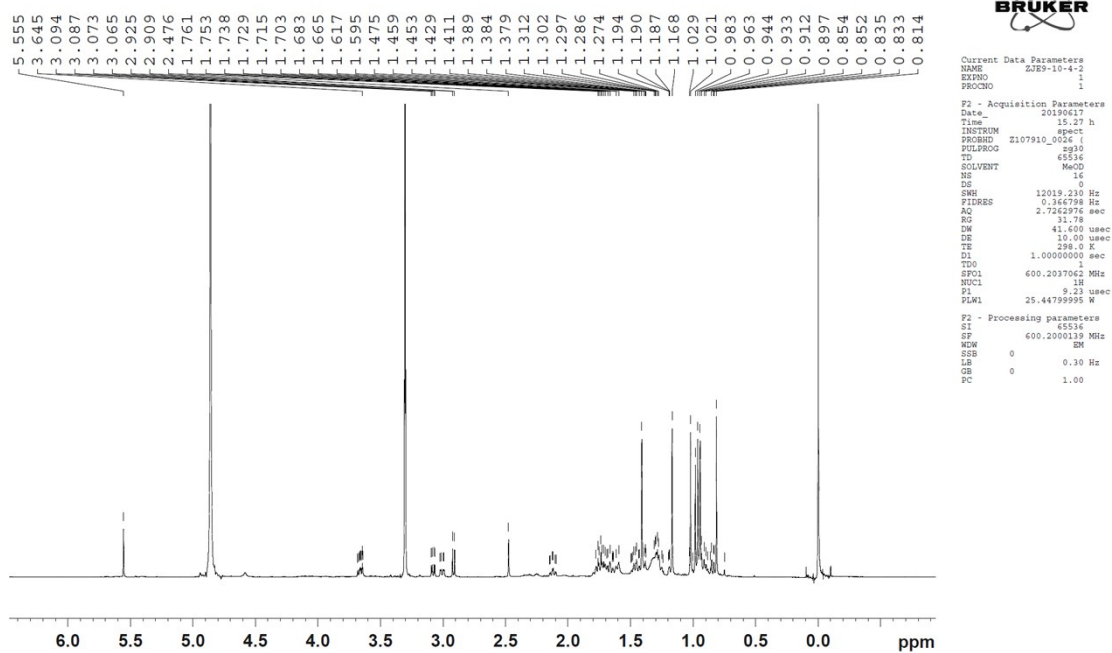


483

484

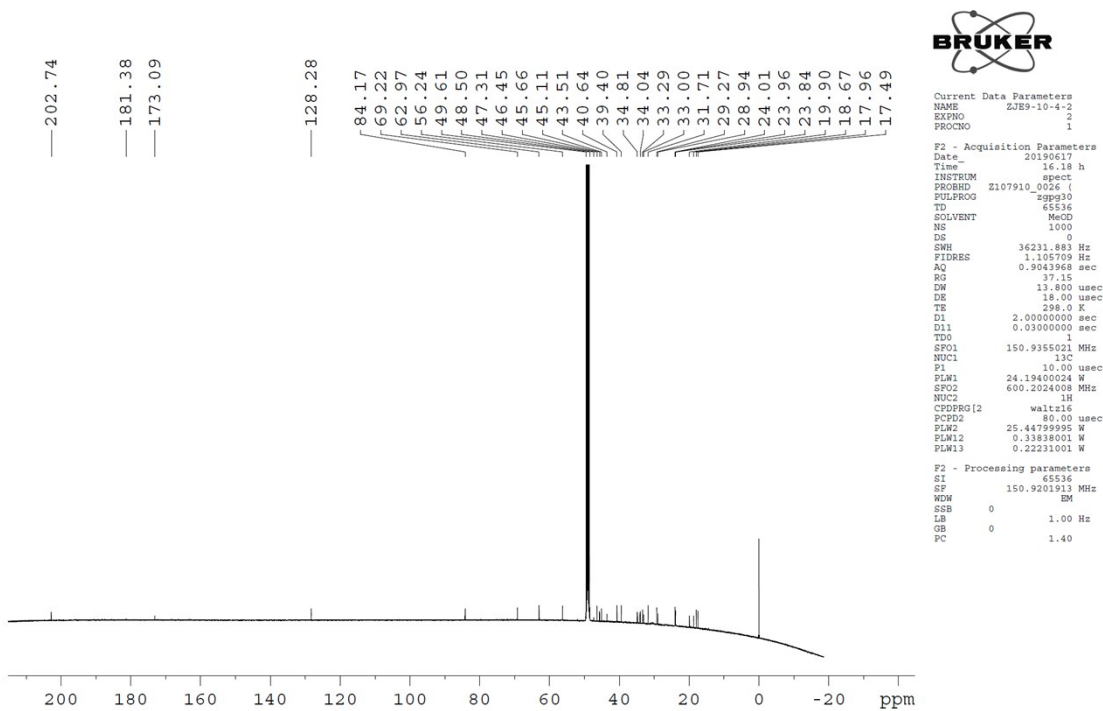
485

Fig. S45. The ESI-Q-Orbitrap MS spectrum of compound **13**



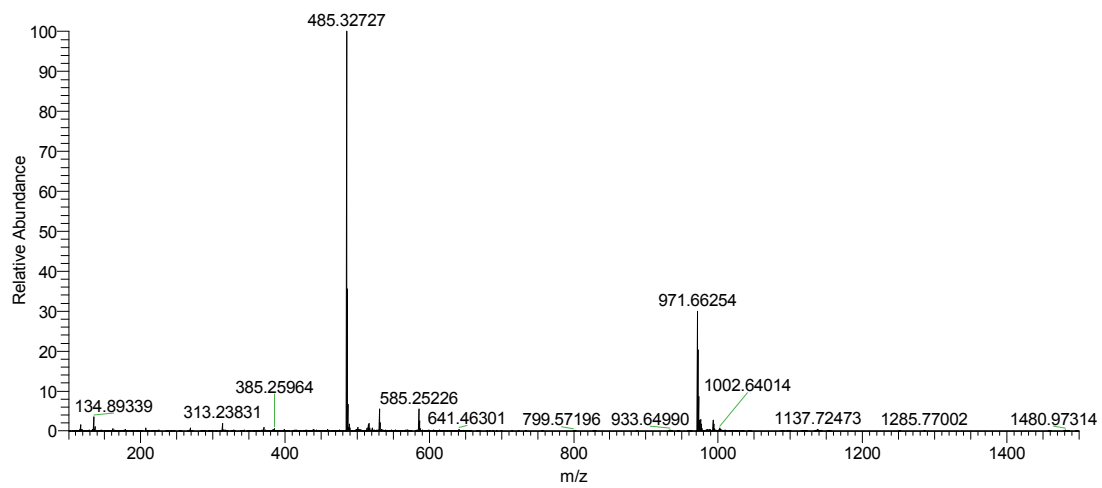
487
488
489

Fig. S46. ¹H NMR (600MHz, CD₃OD) spectrum of compound 14



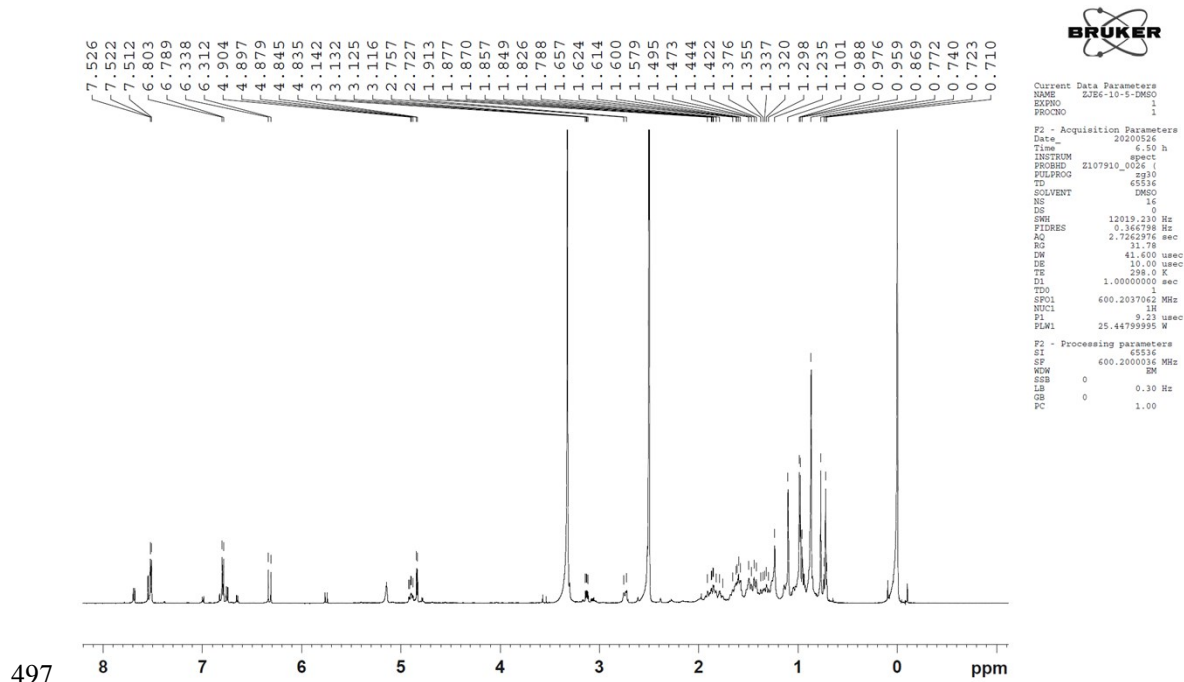
490
491
492

Fig. S47. ¹³C NMR (150MHz, CD₃OD) spectrum of compound 14



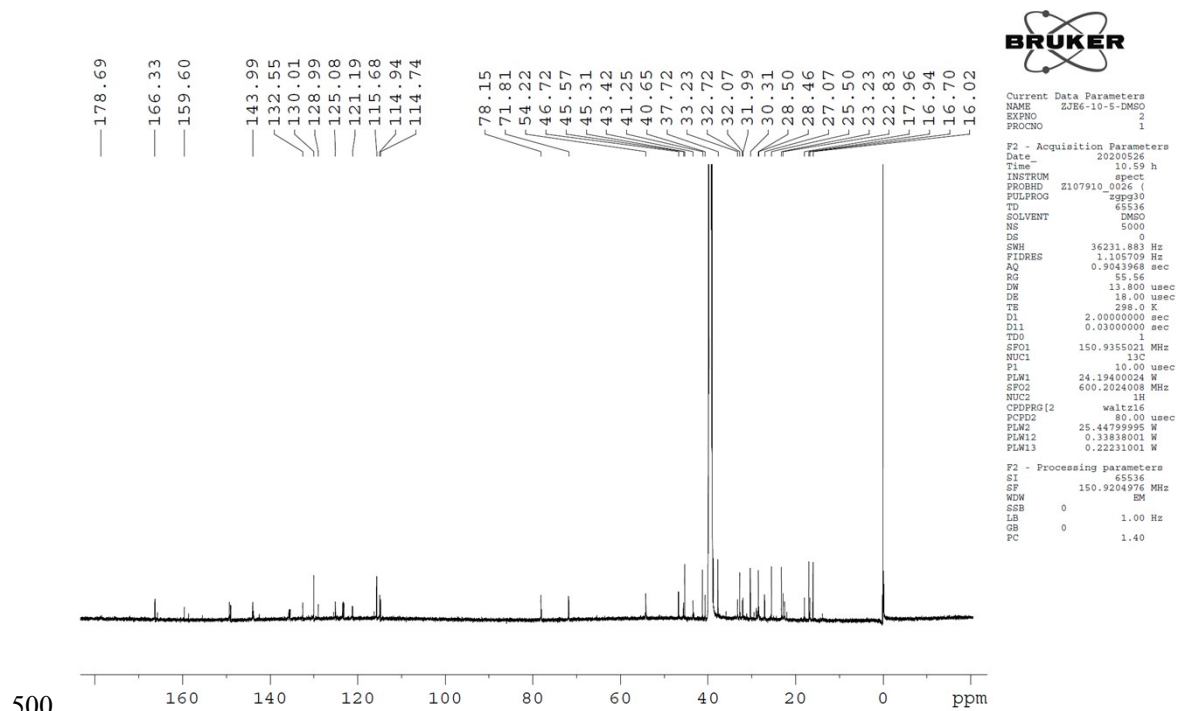
493
494
495

Fig. S48. The ESI-Q-Orbitrap MS spectrum of compound **14**



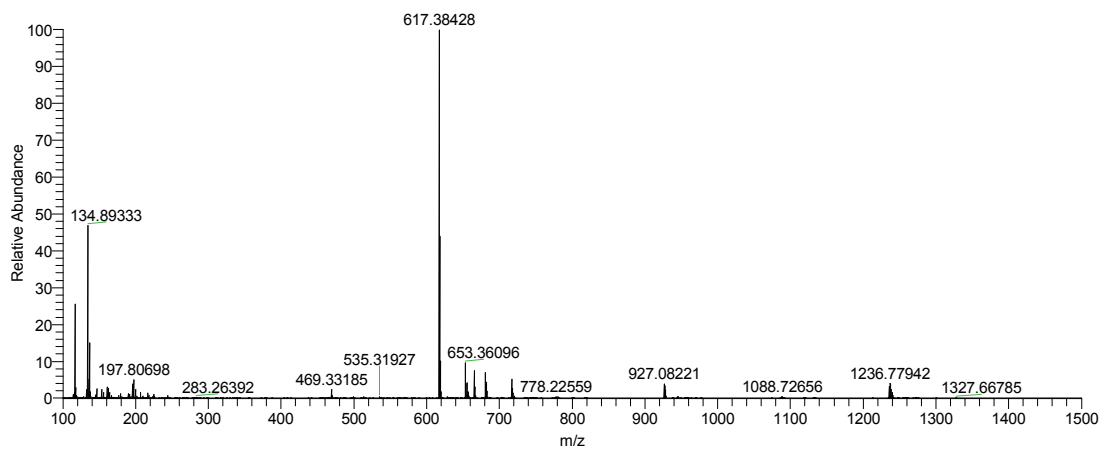
497
498
499

Fig. S49. ¹H NMR (600MHz, DMSO-*d*₆) spectrum of compound 15



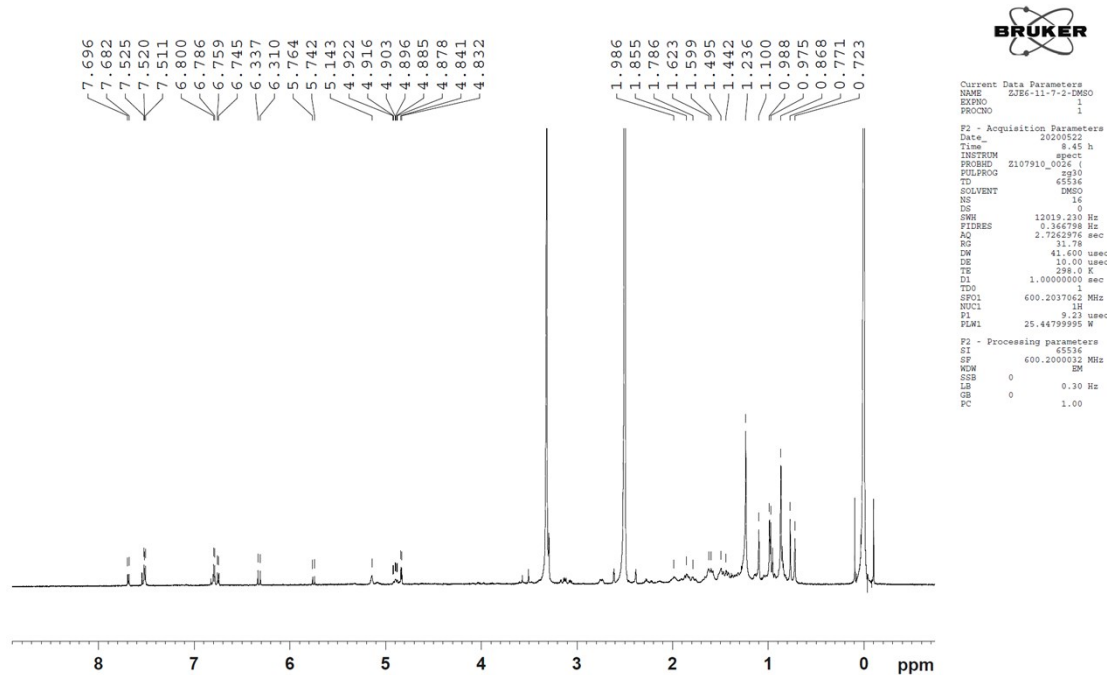
500
501
502

Fig. S50. ¹³C NMR (150MHz, DMSO-*d*₆) spectrum of compound 15



503
504

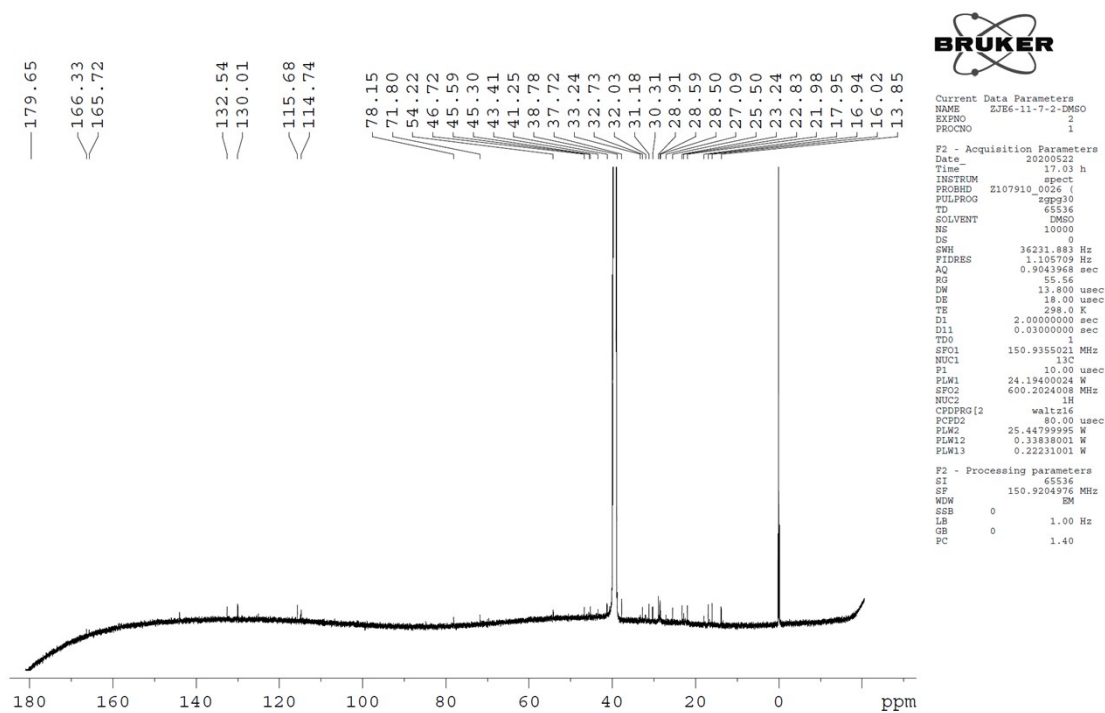
Fig. S51. The ESI-Q-Orbitrap MS spectrum of compound **15**



507

508

509

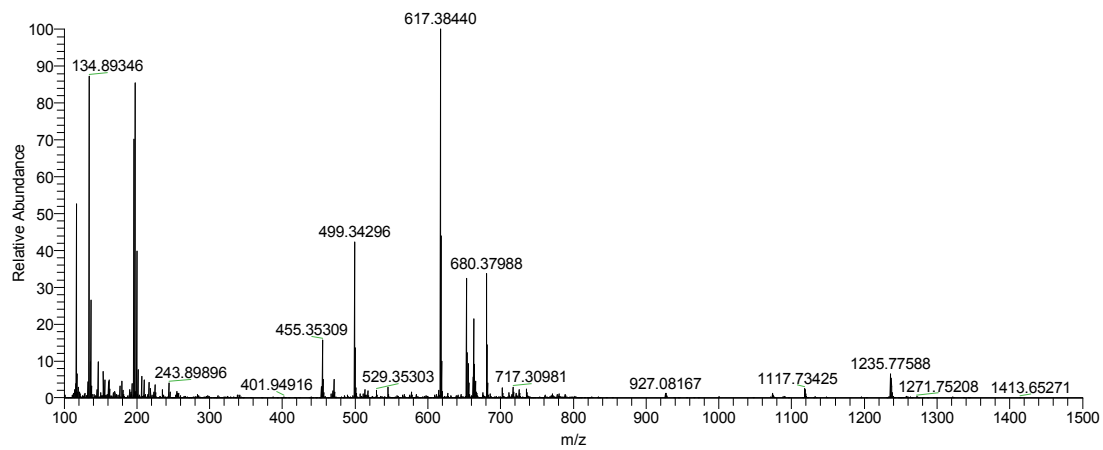
Fig. S52. ^1H NMR (600MHz, $\text{DMSO-}d_6$) spectrum of compound 16

510

511

512

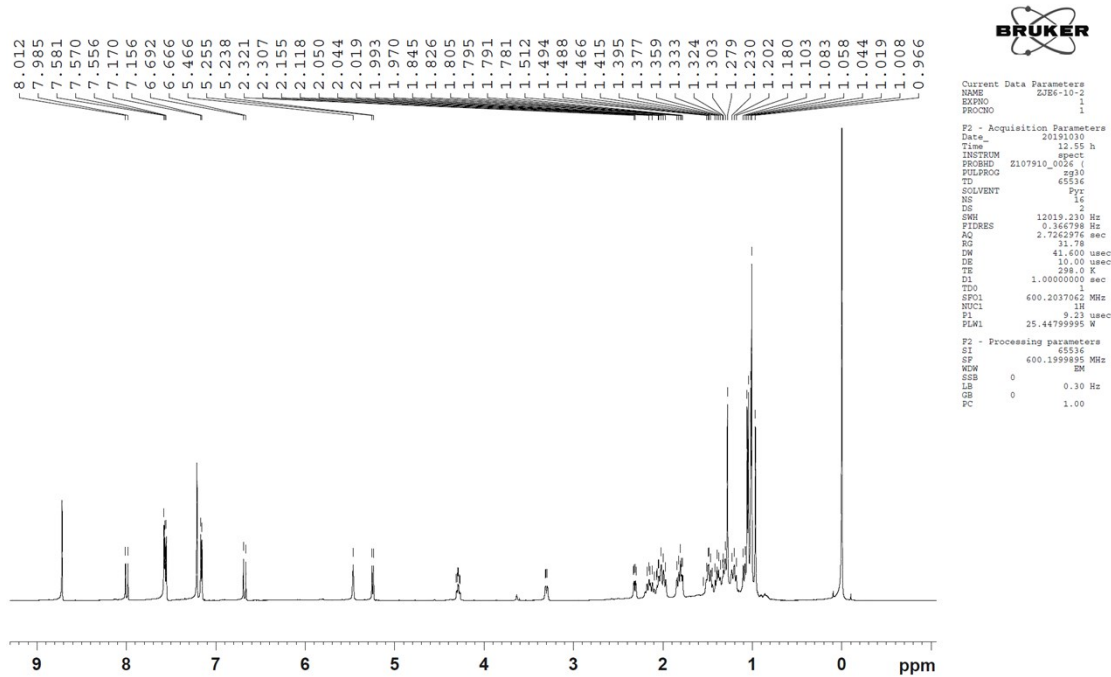
Fig. S53. ^{13}C NMR (150MHz, $\text{DMSO-}d_6$) spectrum of compound 16



513
514
515

Fig. S54. The ESI-Q-Orbitrap MS spectrum of compound **16**

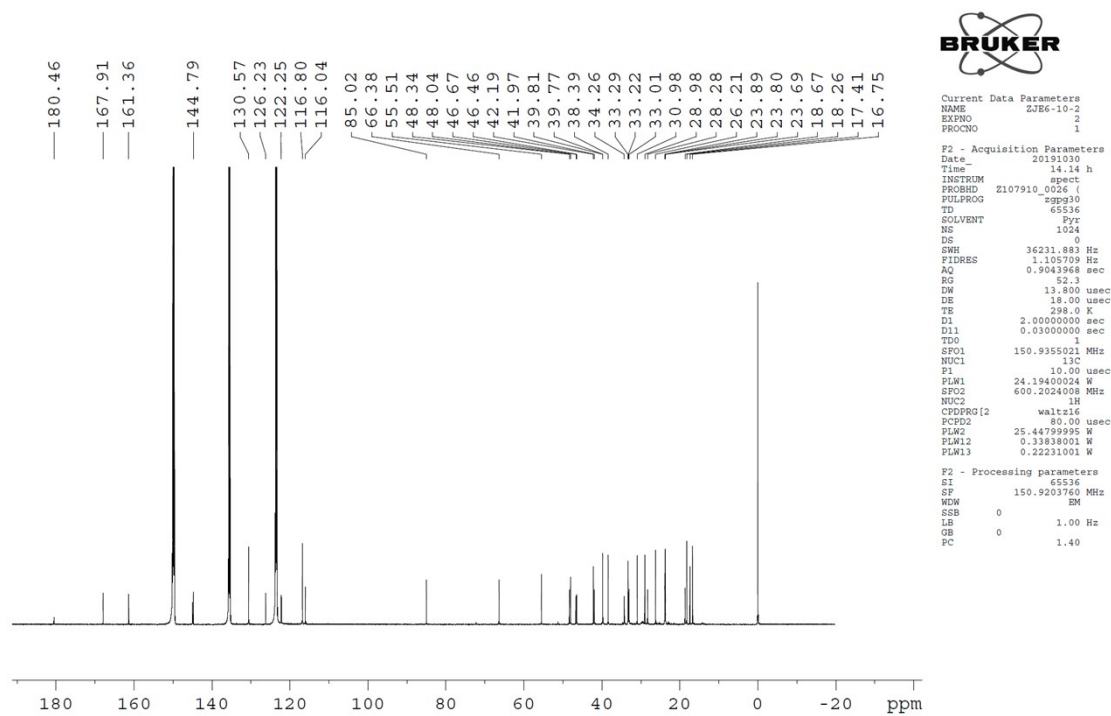
517



518

519

520

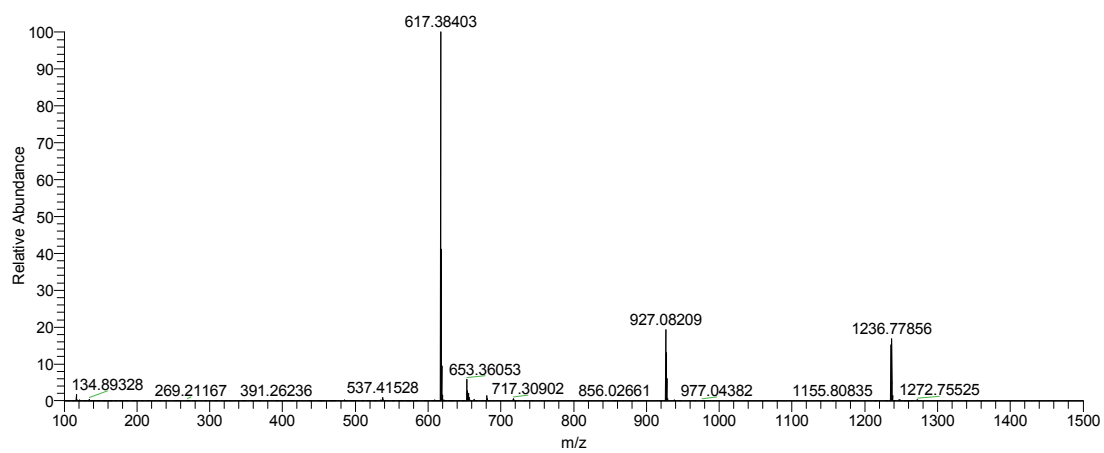
Fig. S55. ^1H NMR (600MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum of compound 17

521

522

523

Fig. S56. ^{13}C NMR (150MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum of compound 17



524
525
526

Fig. S57. The ESI-Q-Orbitrap MS spectrum of compound **17**

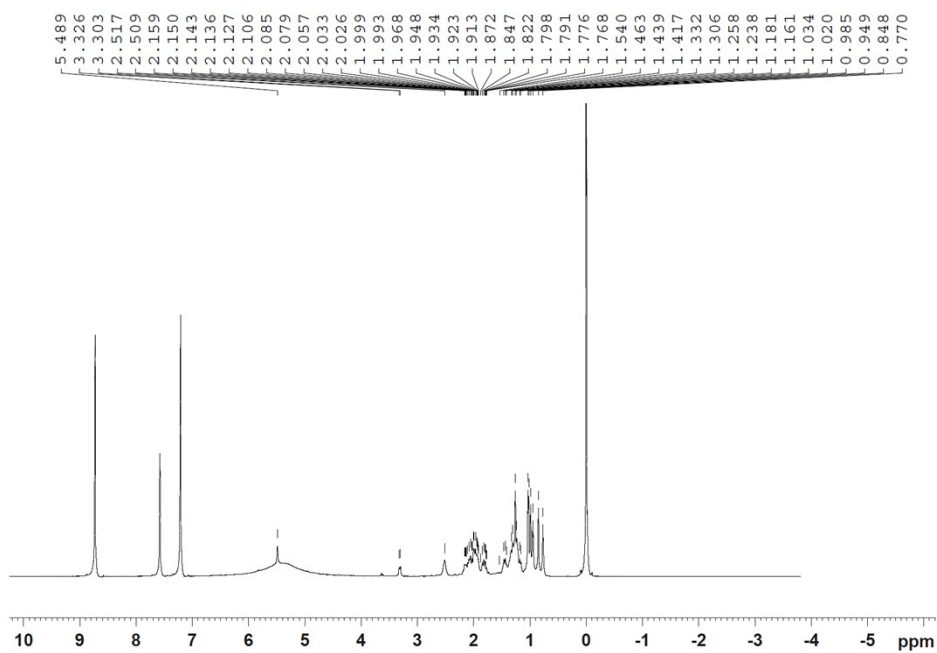


Fig. S58. ¹H NMR (600MHz, C₅D₅N) spectrum of compound 18



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Current Data Parameters
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EXPNO        1
PROCNO       1

F2 - Acquisition Parameters
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Time         9.40 h
INSTRUM     spect
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PULPROG     zg30
TD          65536
SOLVENT     Pyr
NS          16
DS          0
SWH         12019.230 Hz
FIDRES     0.146798 Hz
AQ         2.7262976 sec
RG         16.79
DM         41.600 usec
DE         298.0 K
TE         1.00000000 sec
D1         1.00000000 sec
TDO        0
SFO1       600.2037062 MHz
NUC1       1H
P1         9.23 usec
PLW1       25.4479995 W

F2 - Processing parameters
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SF         600.1999822 MHz
WDW        EM
SSB        0
LB         0.10 Hz
GB         0
PC         1.00
  
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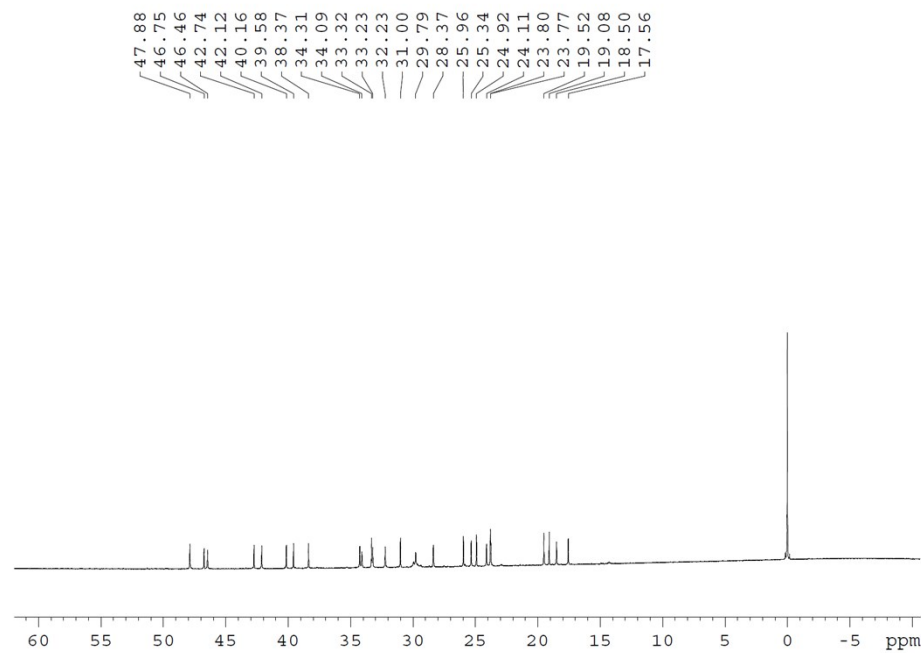


Fig. S59. ¹³C NMR (150MHz, C₅D₅N) spectrum-1 of compound 18

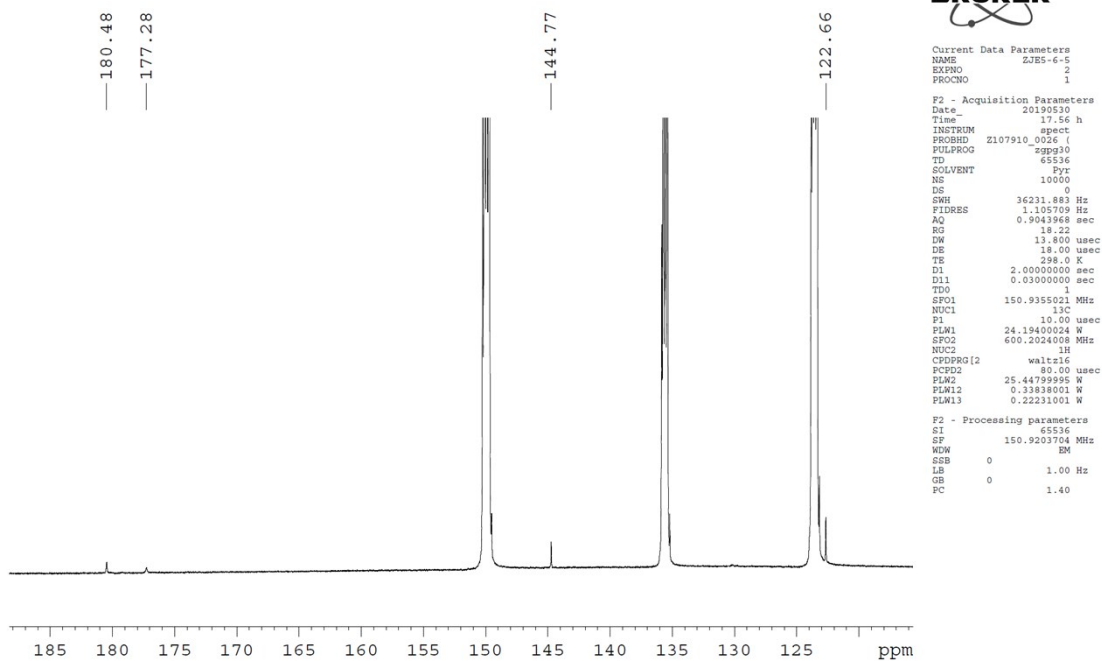


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PROCNO       1

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Time         17.56 h
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PULPROG     zgpg30
TD          65536
SOLVENT     Pyr
NS          10000
DS          0
SWH         36231.883 Hz
FIDRES     1.105709 Hz
AQ         0.8043968 sec
RG         18.22
DM         12.800 usec
DE         18.00 usec
TE         298.0 K
D1         2.00000000 sec
D11        0.03000000 sec
TDO        1
SFO1       150.9355021 MHz
NUC1       13C
P1         10.00 usec
PLW1       24.19400024 W
SFO2       600.2024008 MHz
NUC2       1H
CPDPRG[2]   waltz16
PCPD2       80.00 usec
PLW2       25.44799995 W
PLW12      0.33838001 W
PLW13      0.22231001 W

F2 - Processing parameters
SI         65536
SF         150.9203704 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
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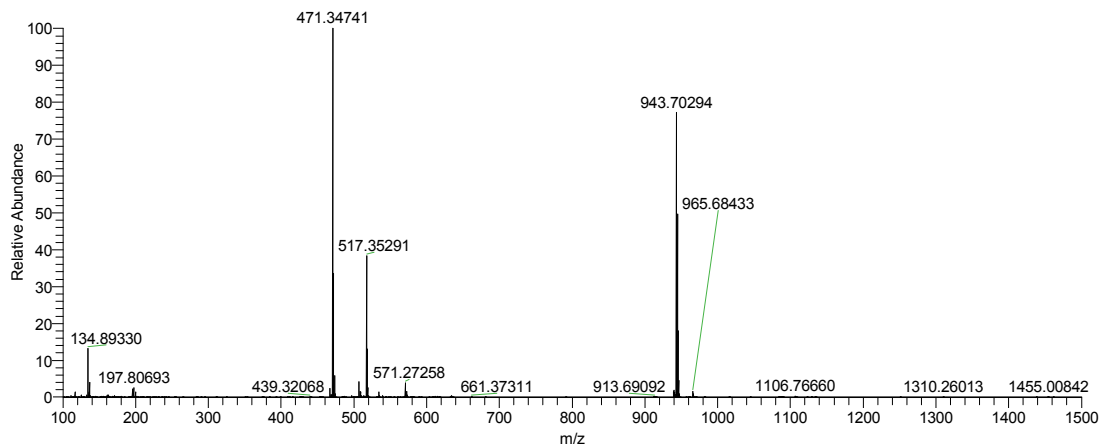


534

535

Fig. S60. ^{13}C NMR (150MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum-2 of compound **18**

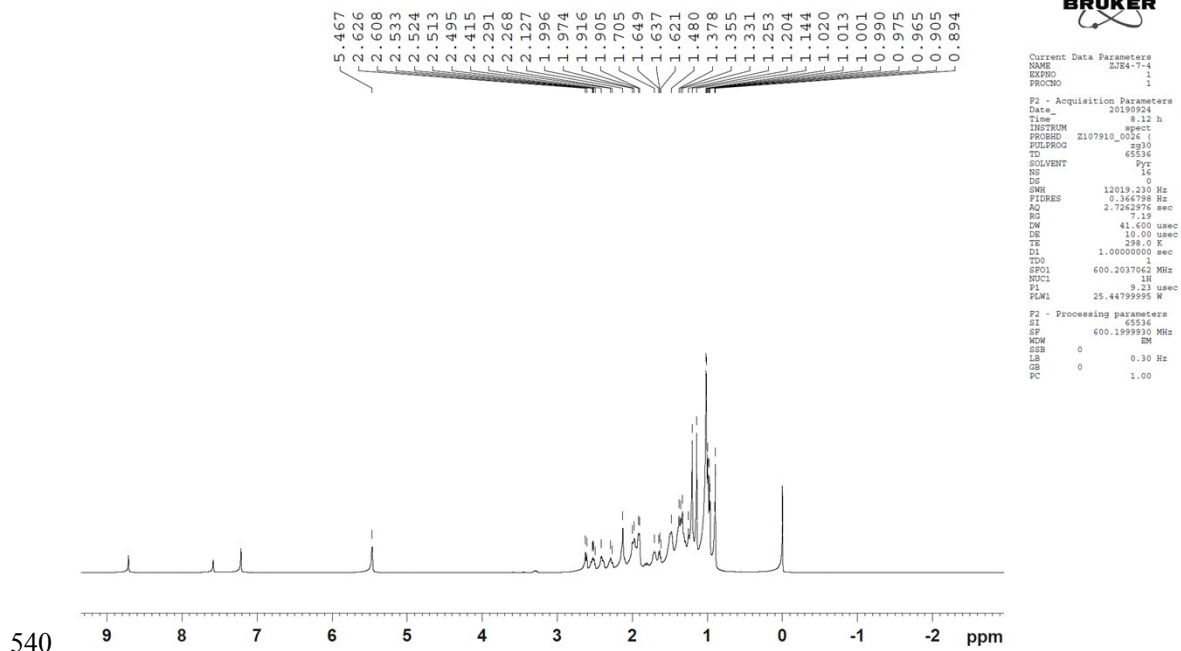
536



537

538

Fig. S61. The ESI-Q-Orbitrap MS spectrum of compound **18**



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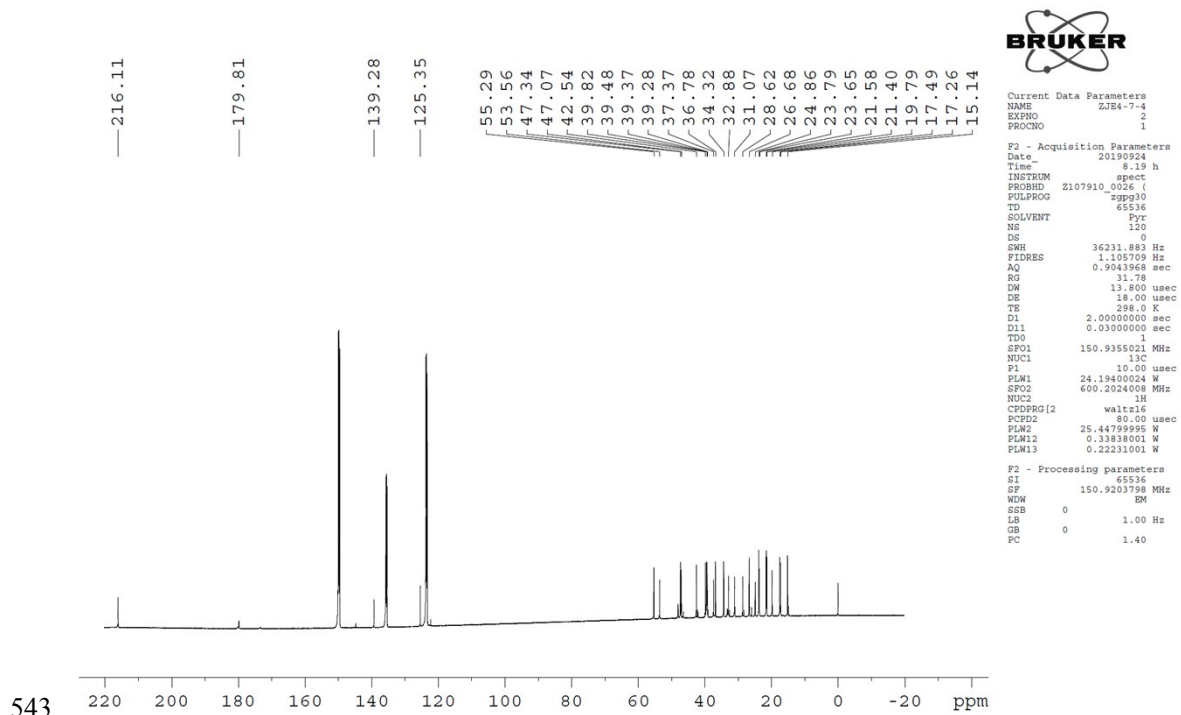
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EXPNO    1
PROCNO   1

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Time     8.12 h
INSTRUM  spect
PROBHD   Z107910_0026 (
PULPROG  zg30
TD        65536
SOLVENT  Pyr
NS        16
DS        0
SWH       12019.230 Hz
FIDRES    0.264798 Hz
AQ        2.7262976 sec
RG        7.19
DW        41.600 usec
DE        10.00 usec
TE        298.0 K
TD0       1.00000000 sec
SFO1      600.2037062 MHz
NUC1      1H
P1         9.23 usec
PLW1      25.4479995 W

F2 - Processing parameters
SI         65536
SF         600.1999910 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
  
```

540
541
542

Fig. S62. ¹H NMR (600MHz, C₅D₅N) spectrum of compound 19



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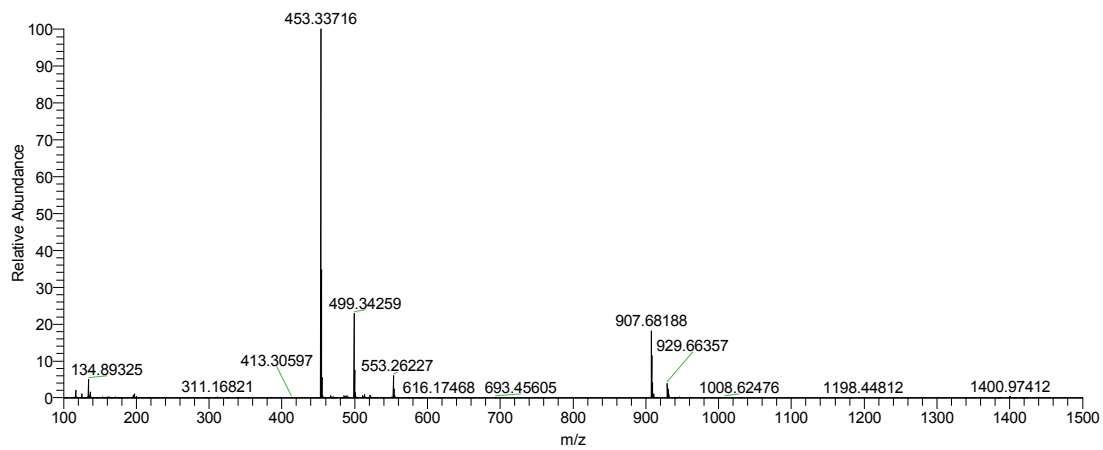
Current Data Parameters
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EXPNO    2
PROCNO   1

F2 - Acquisition Parameters
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PULPROG  zgpg30
TD        65536
SOLVENT  Pyr
NS        120
DS        0
SWH       36231.883 Hz
FIDRES    1.105709 Hz
AQ        0.3043968 sec
RG        31.78
DW        13.800 usec
DE        18.00 usec
TE        298.0 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0       1
SFO1      150.9355021 MHz
NUC1      13C
P1        10.00 usec
PLW1      24.19400024 W
SFO2      600.2024008 MHz
NUC2      1H
CPDPRG2  waltz16
PCPD2     80.00 usec
PLW2     25.4479995 W
PLW12    0.33838001 W
PLW13    0.22231001 W

F2 - Processing parameters
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SF         150.9203798 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
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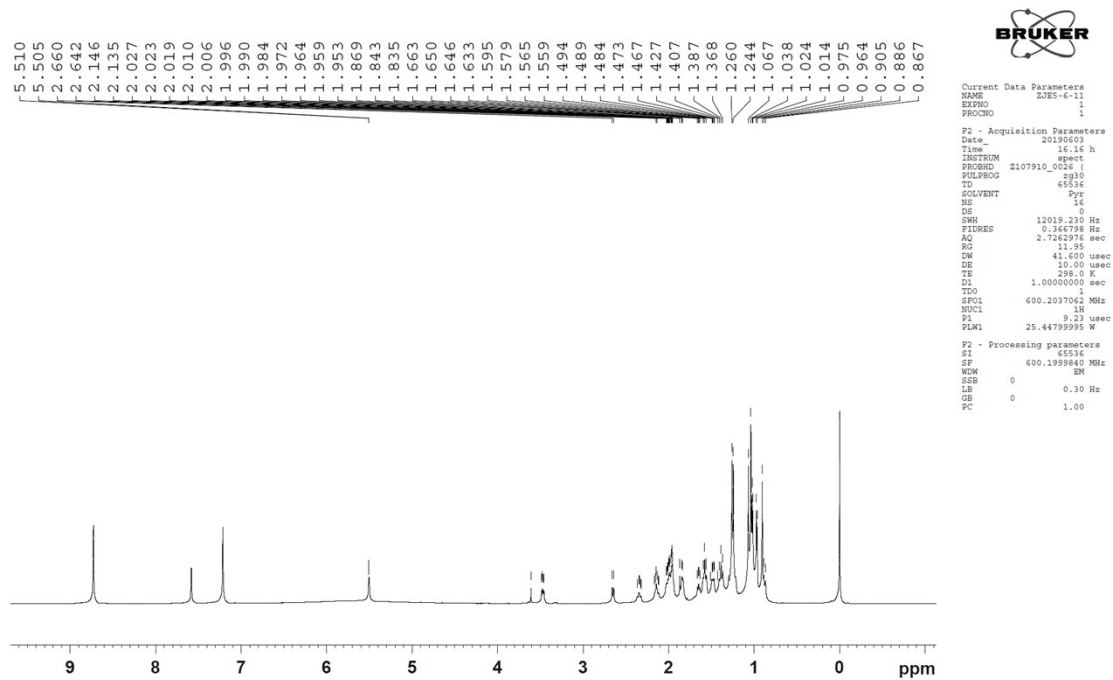
543
544
545

Fig. S63. ¹³C NMR (150MHz, C₅D₅N) spectrum of compound 19



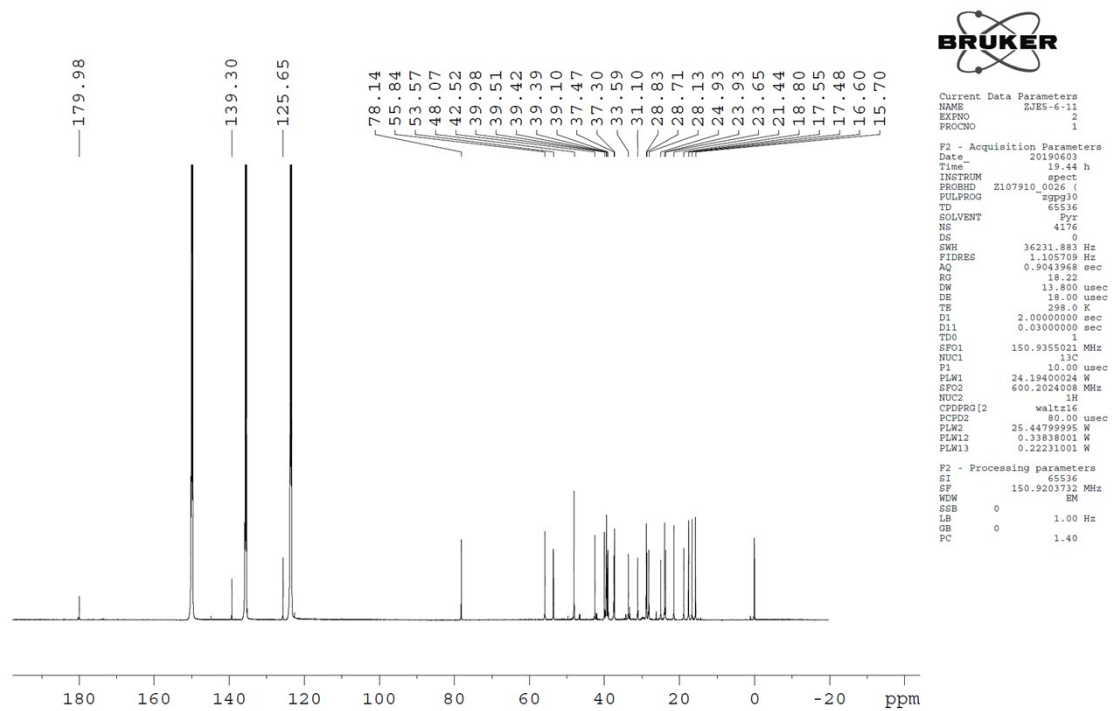
546
547
548

Fig. S64. The ESI-Q-Orbitrap MS spectrum of compound **19**



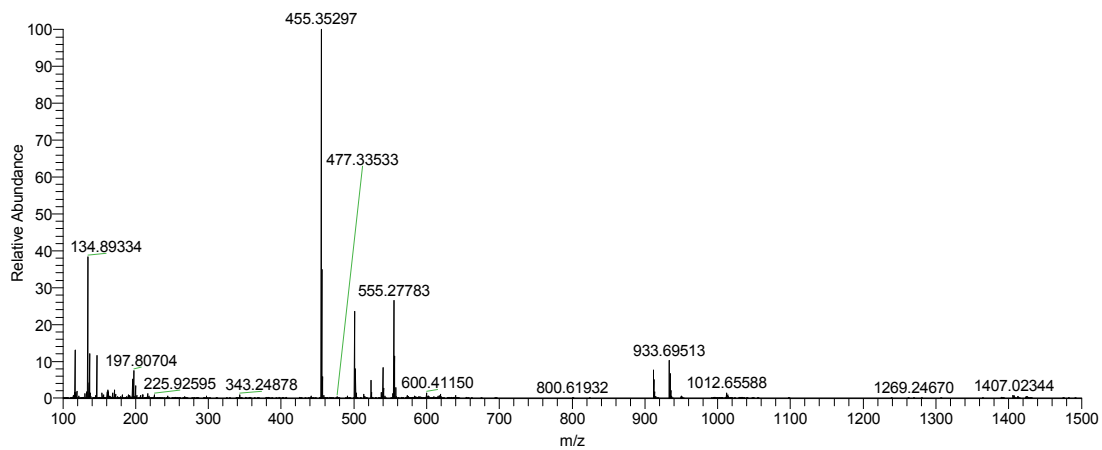
550
551
552

Fig. S65. ^1H NMR (600MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum of compound **20**



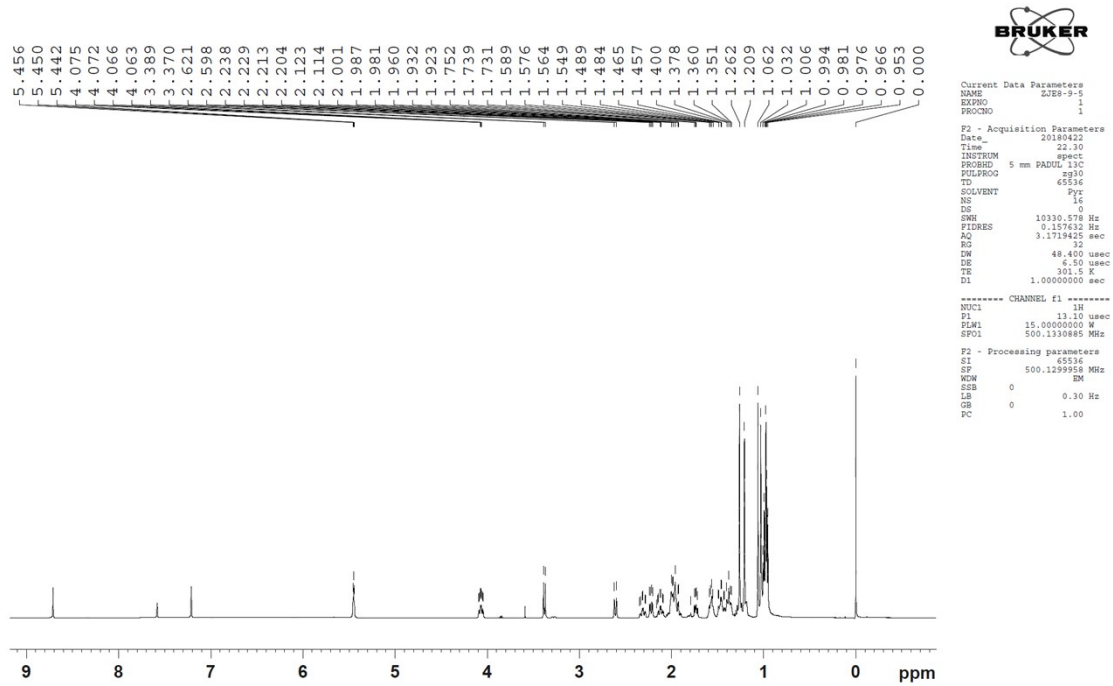
553
554
555

Fig. S66. ^{13}C NMR (150MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum of compound **20**



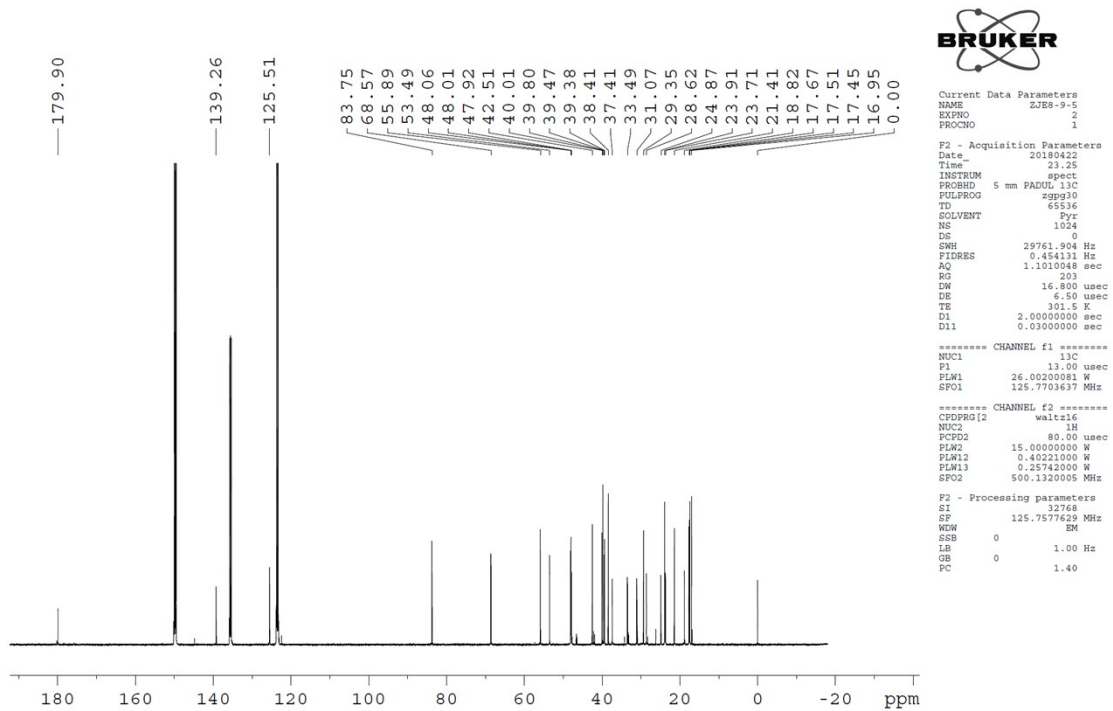
556
557
558

Fig. S67. The ESI-Q-Orbitrap MS spectrum of compound **20**



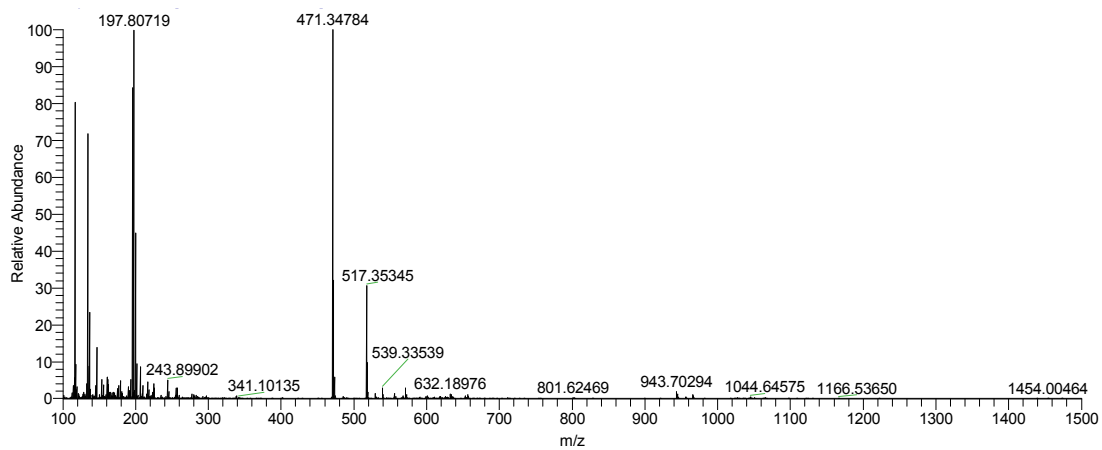
560
561
562

Fig. S68. ¹H NMR (500MHz, C₅D₅N) spectrum of compound 21



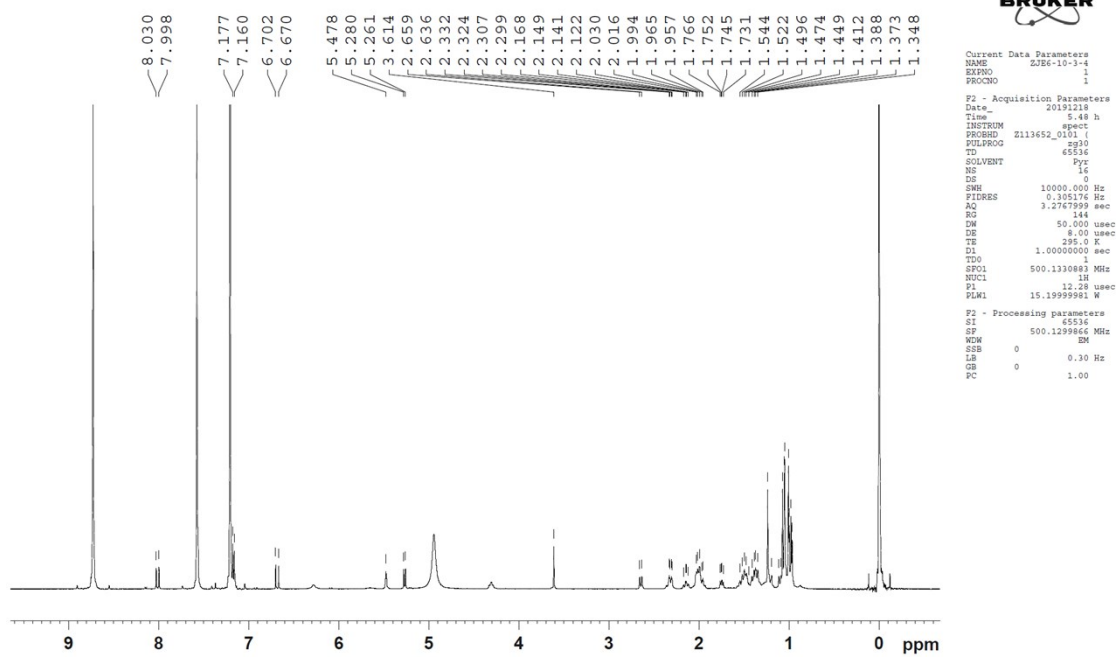
563
564
565

Fig. S69. ¹³C NMR (125MHz, C₅D₅N) spectrum of compound 21



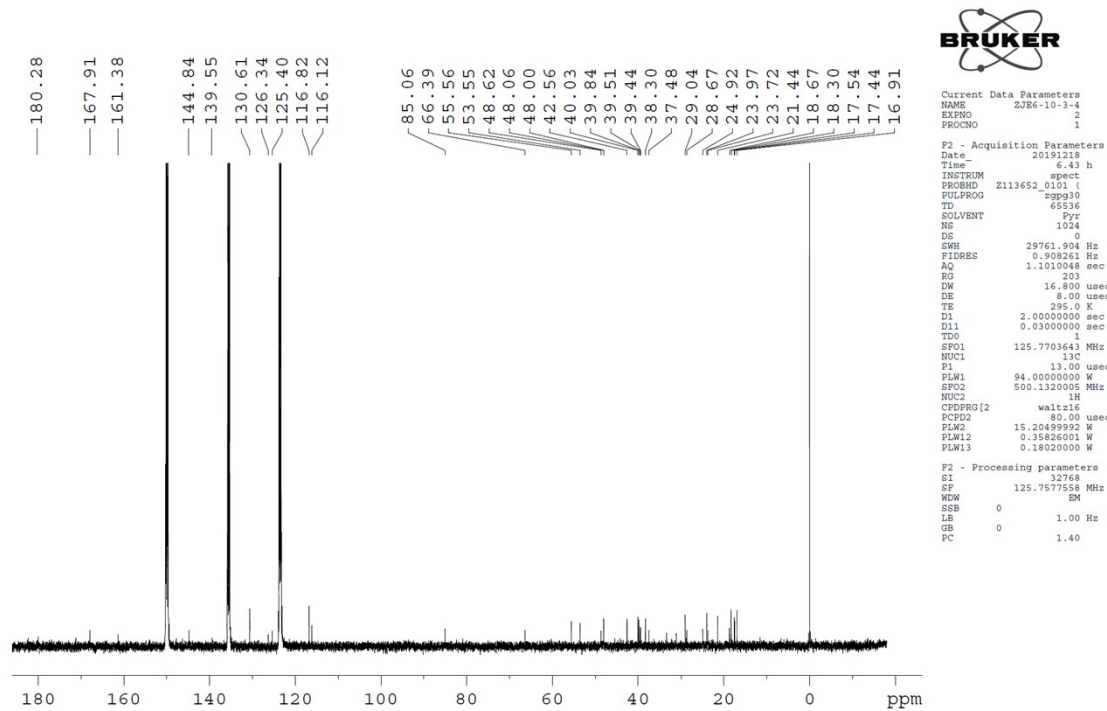
566
567
568

Fig. S70. The ESI-Q-Orbitrap MS spectrum of compound **21**



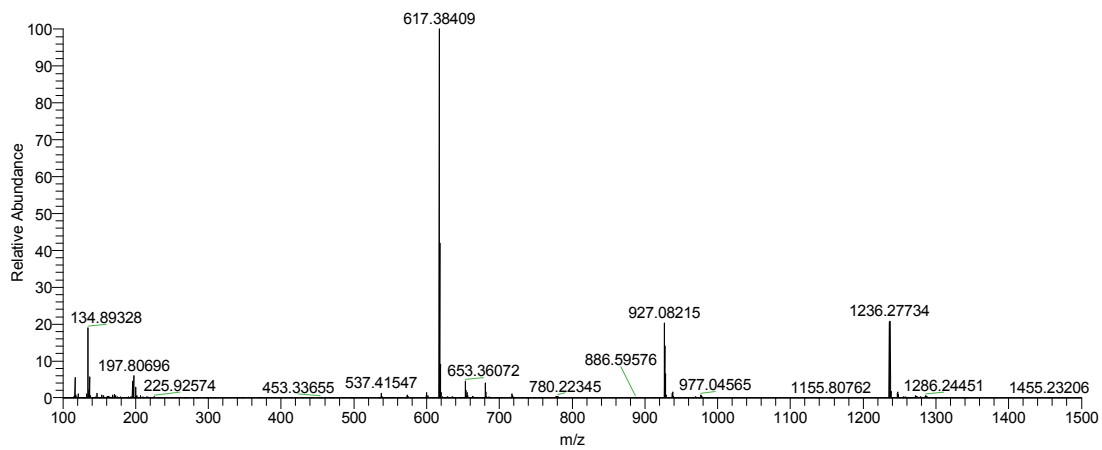
570
571
572

Fig. S71. ¹H NMR (500MHz, C₅D₅N) spectrum of compound 22



573
574
575

Fig. S72. ¹³C NMR (125MHz, C₅D₅N) spectrum of compound 22



576

577

Fig. S73. The ESI-Q-Orbitrap MS spectrum of compound **22**

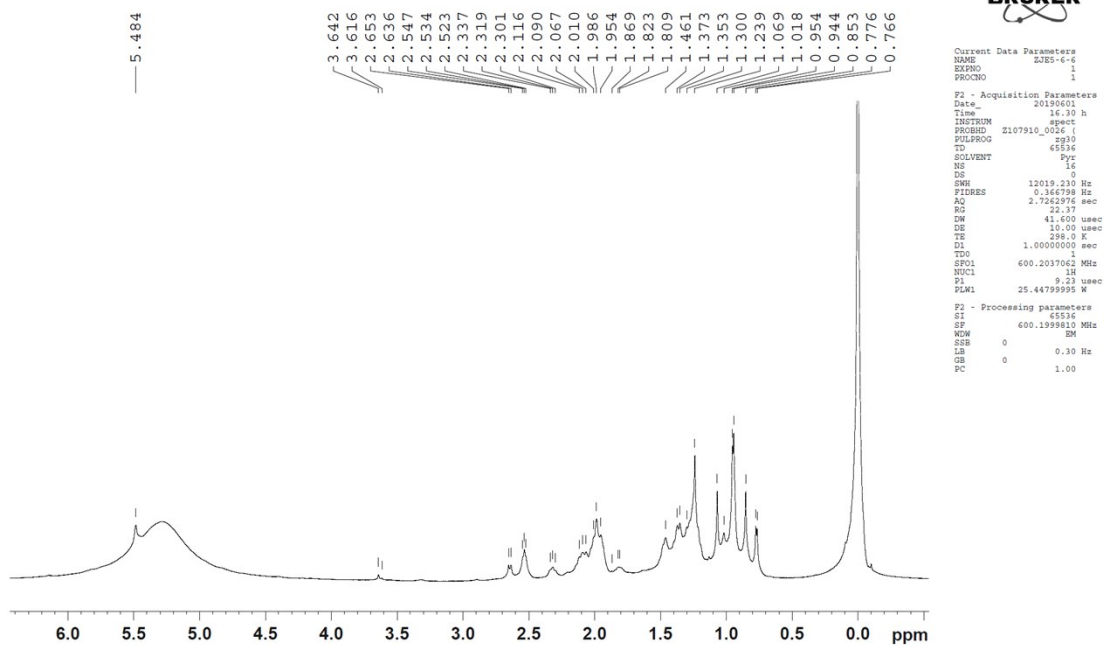


Fig. S74. ^1H NMR (600MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum of compound 23

580

581

582

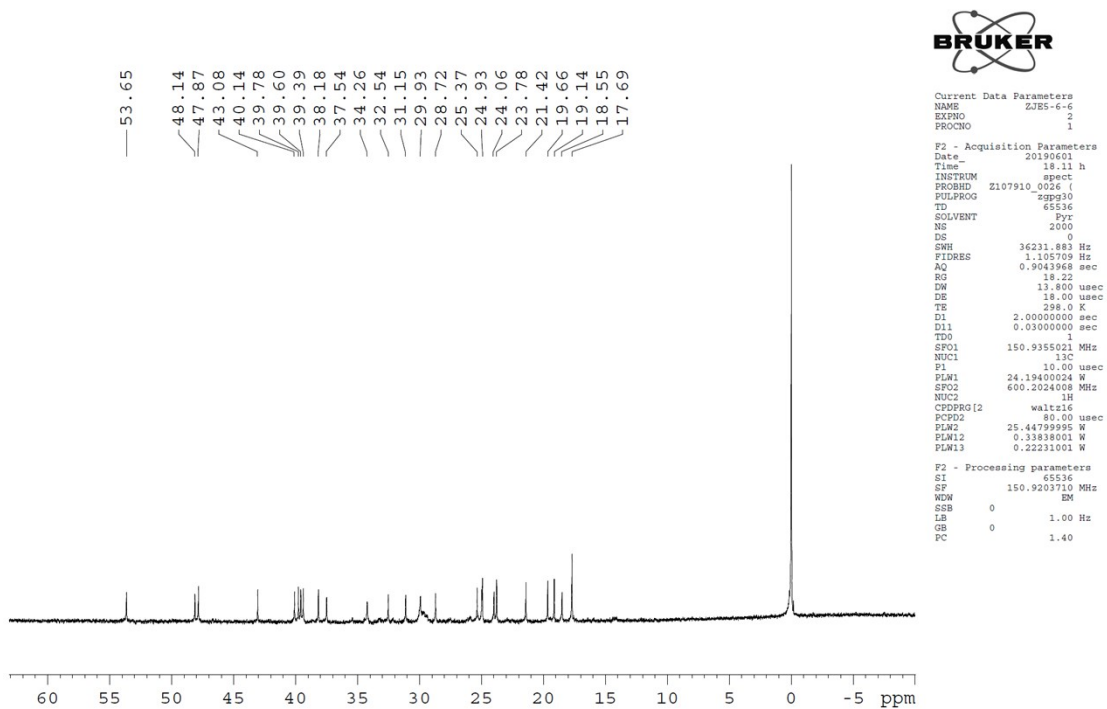
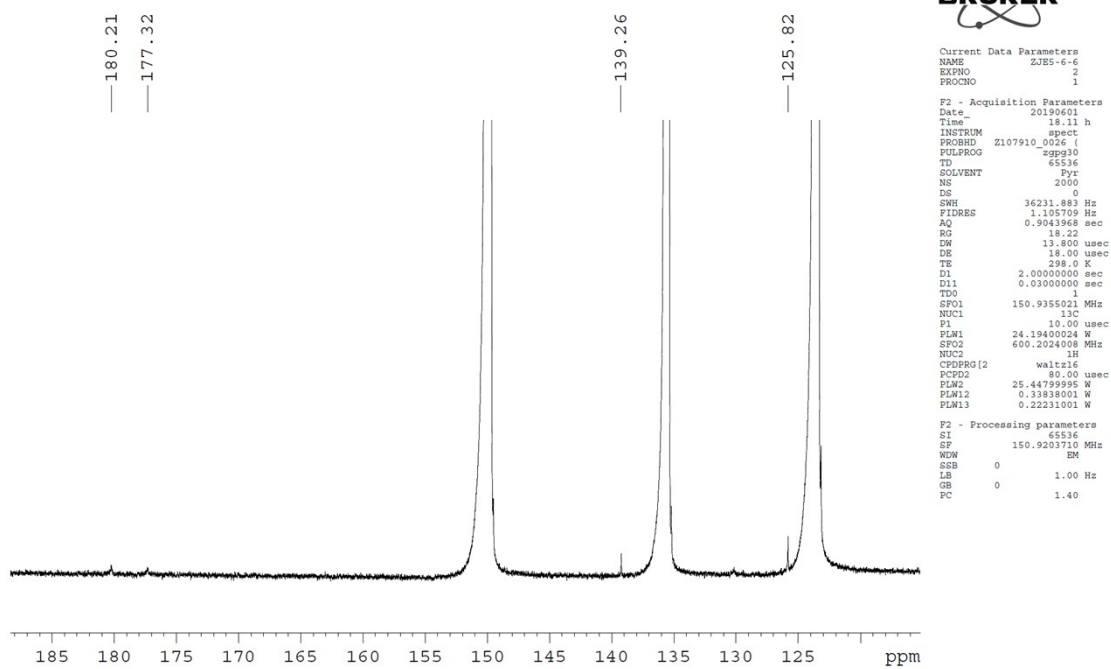


Fig. S75. ^{13}C NMR (150MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum-1 of compound 23

583

584

585

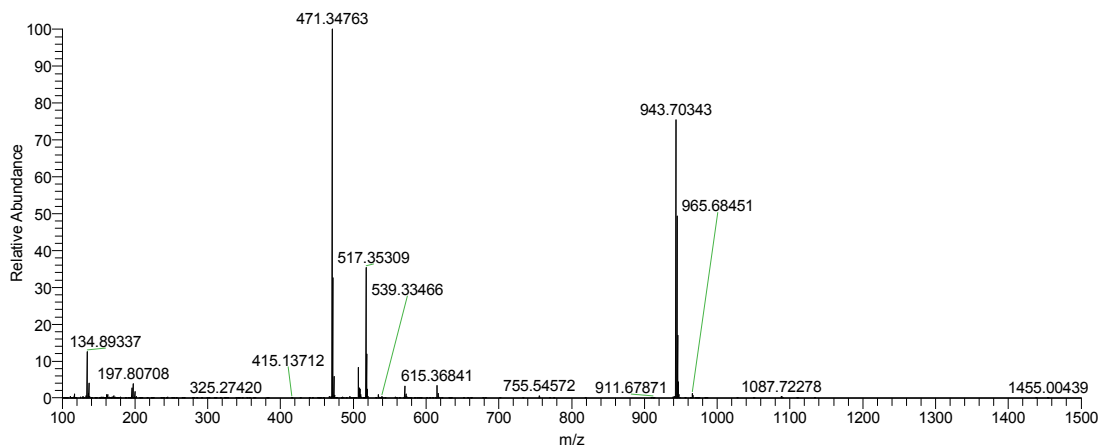


586

587

588

Fig. S76. ^{13}C NMR (150MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum-2 of compound 23



589

590

Fig. S77. The ESI-Q-Orbitrap MS spectrum of compound 23

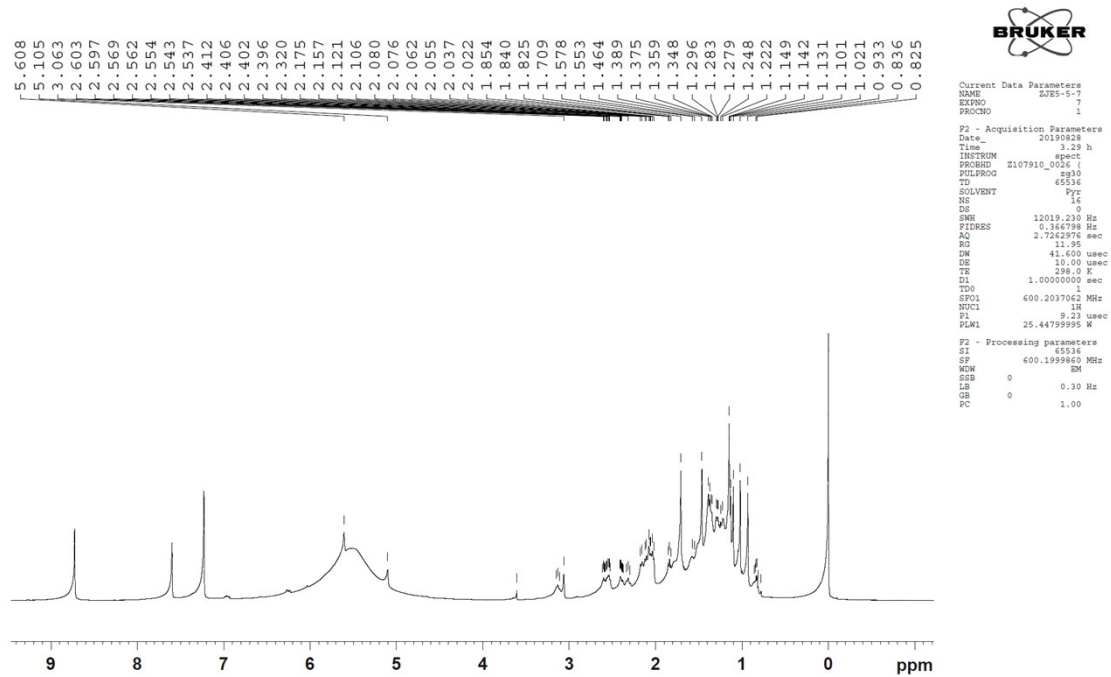


Fig. S78. ¹H NMR (600MHz, C₅D₅N) spectrum of compound 24

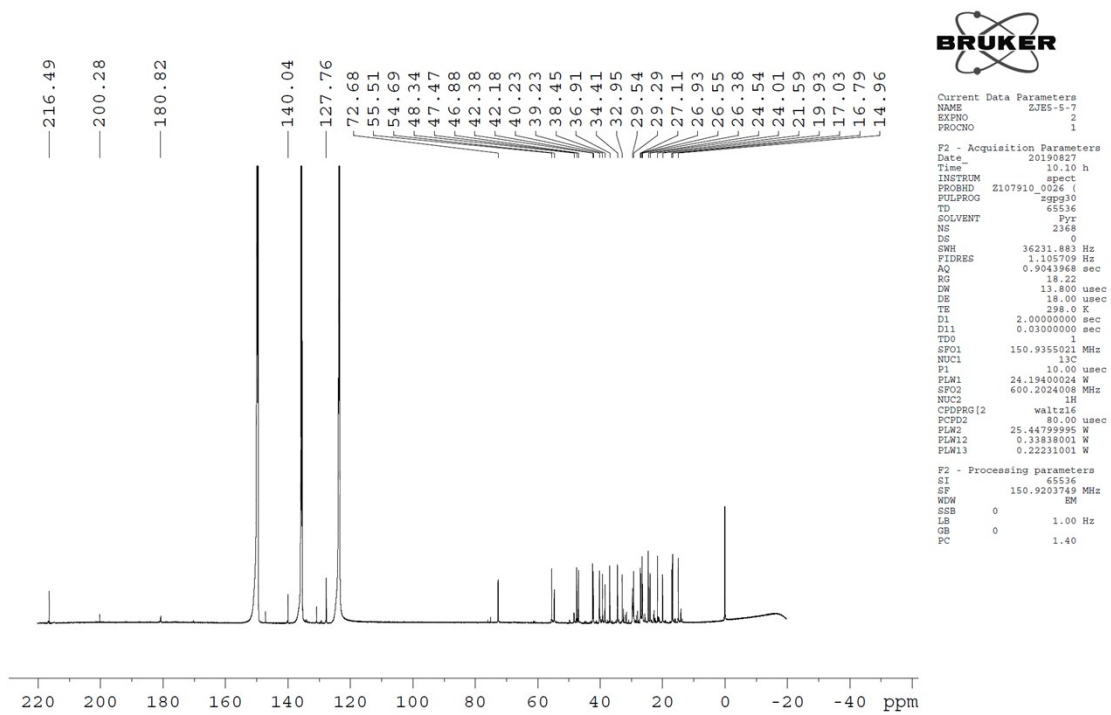
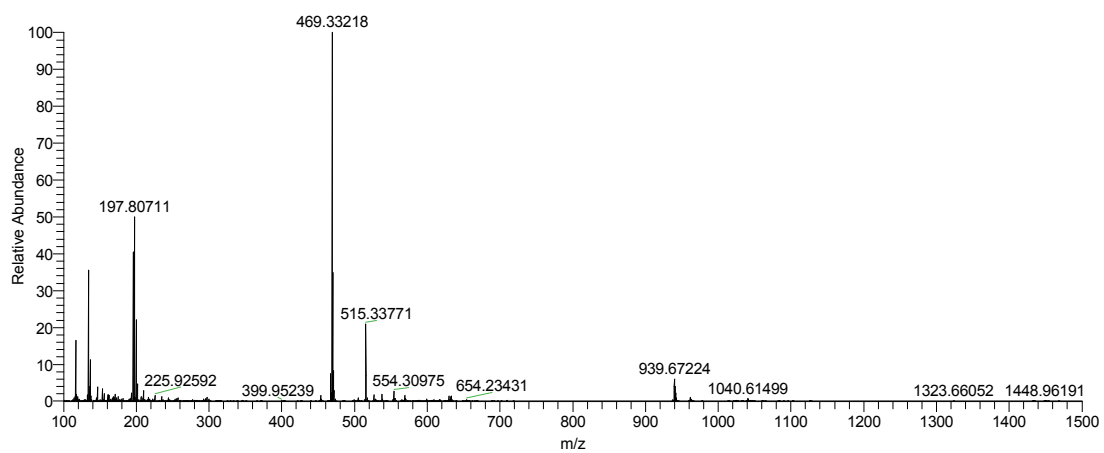


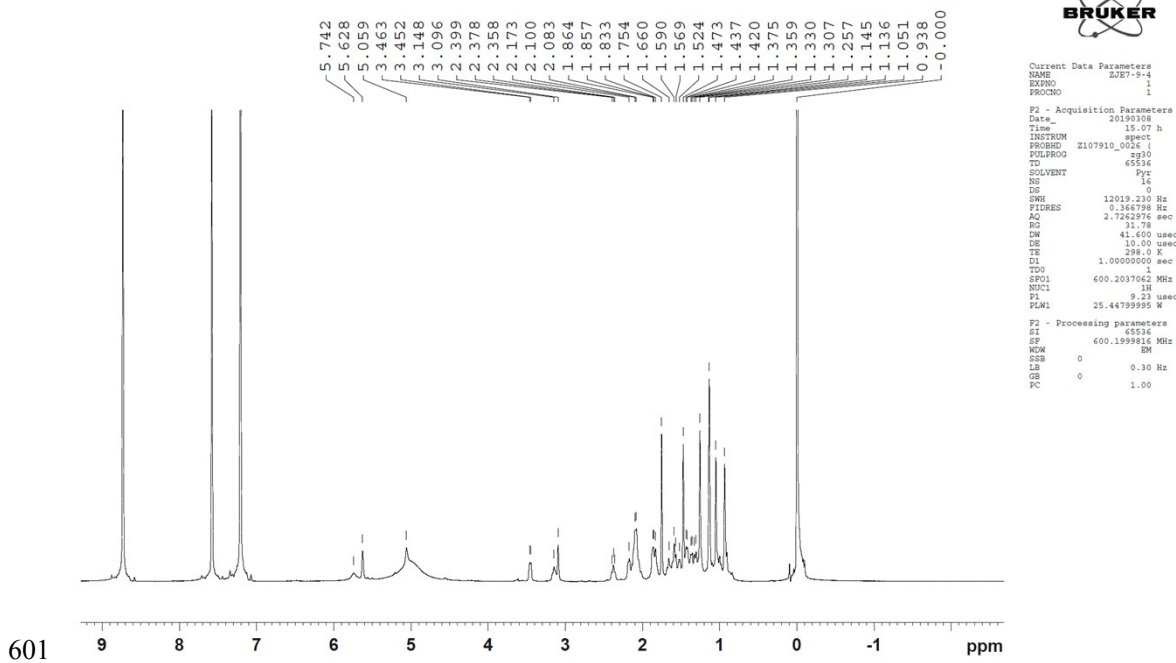
Fig. S79. ¹³C NMR (150MHz, C₅D₅N) spectrum of compound 24



598

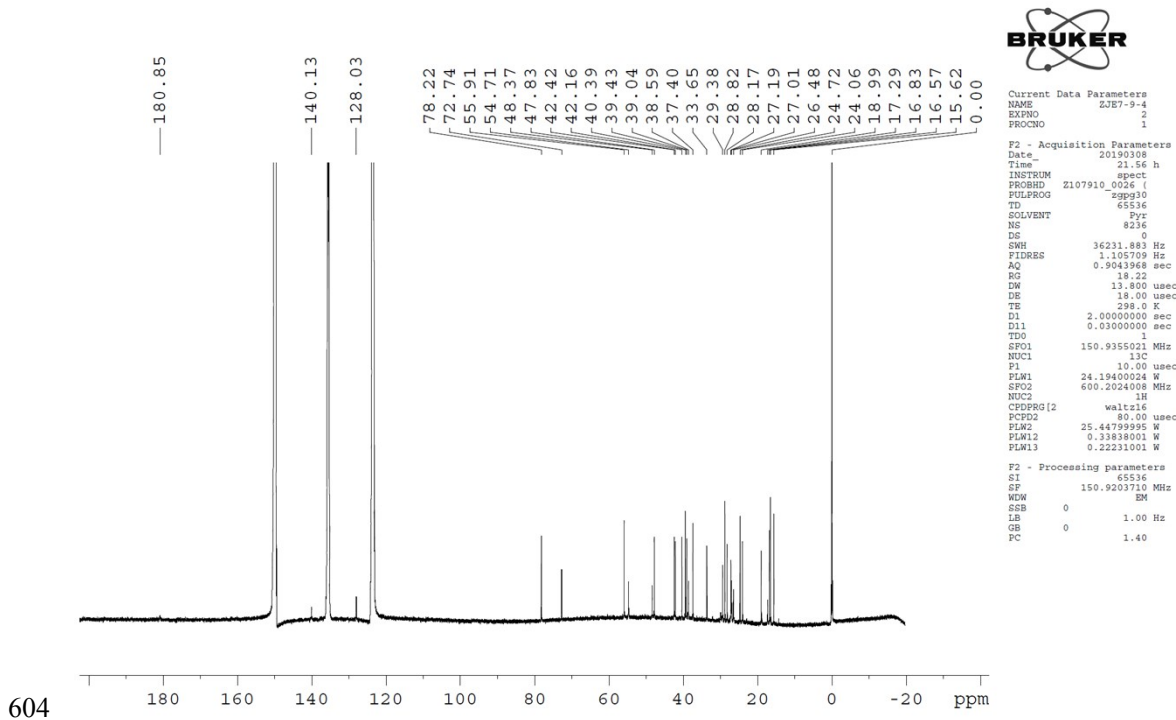
599

Fig. S80. The ESI-Q-Orbitrap MS spectrum of compound **24**



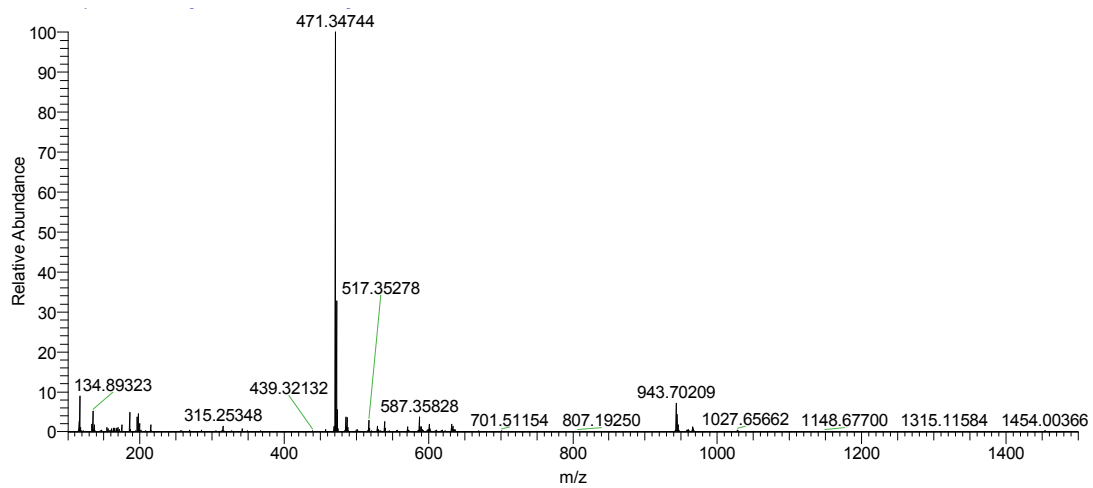
601
602
603

Fig. S81. ¹H NMR (600MHz, C₅D₅N) spectrum of compound 25



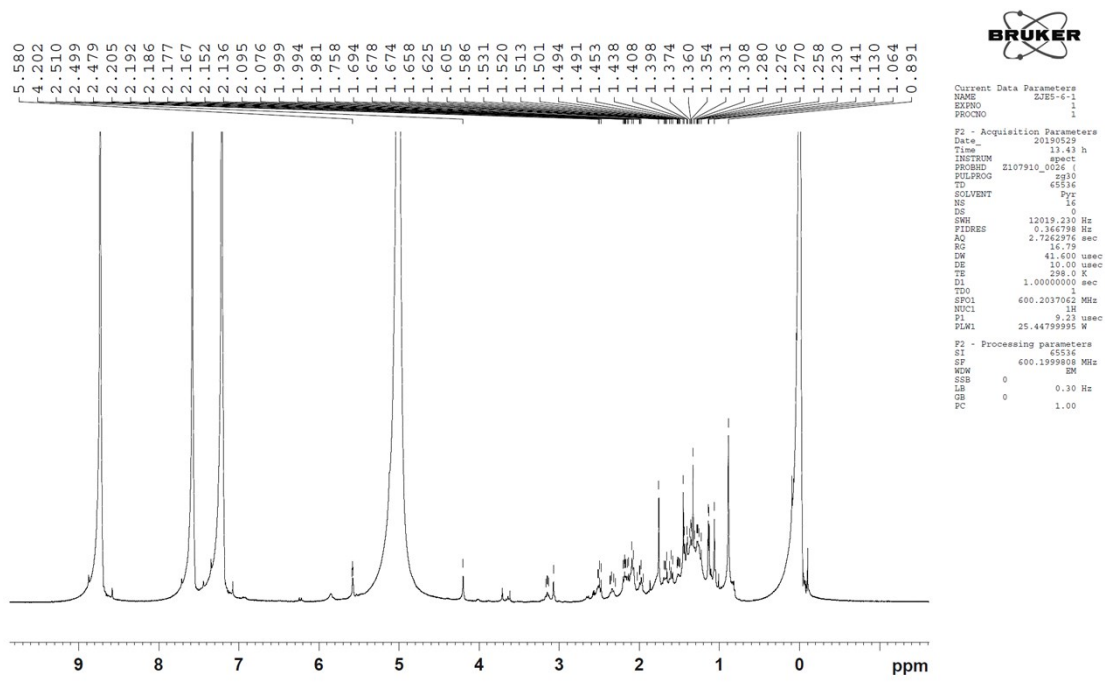
604
605
606

Fig. S82. ¹³C NMR (150MHz, C₅D₅N) spectrum of compound 25



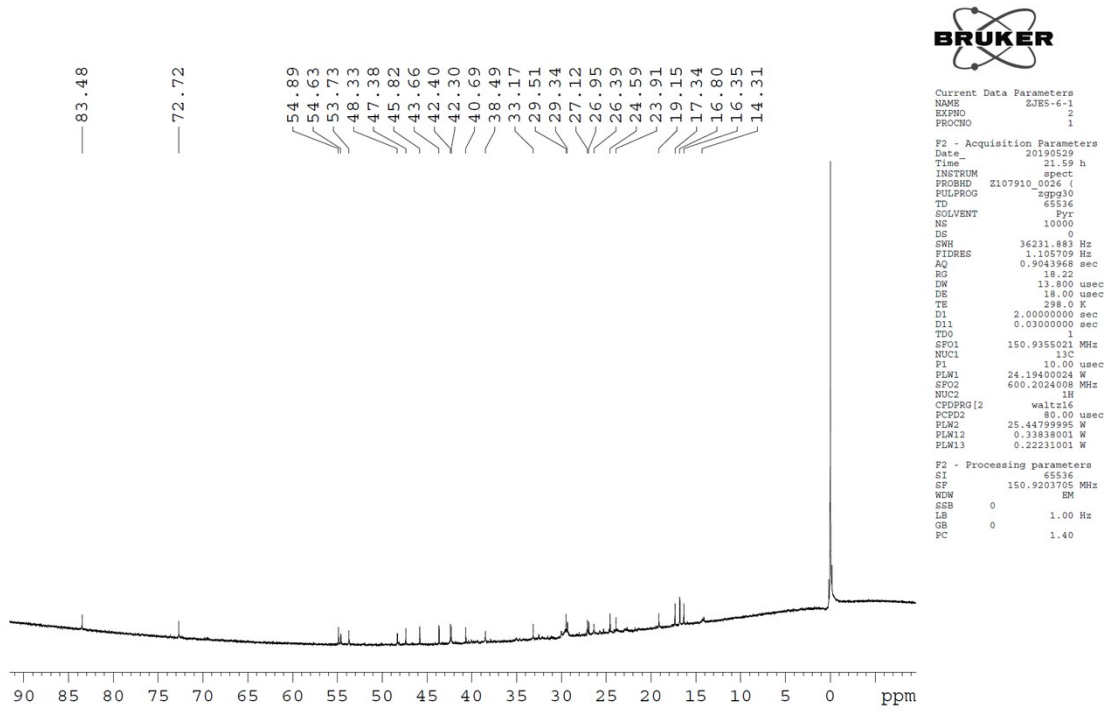
607
608

Fig. S83. The ESI-Q-Orbitrap MS spectrum of compound **25**



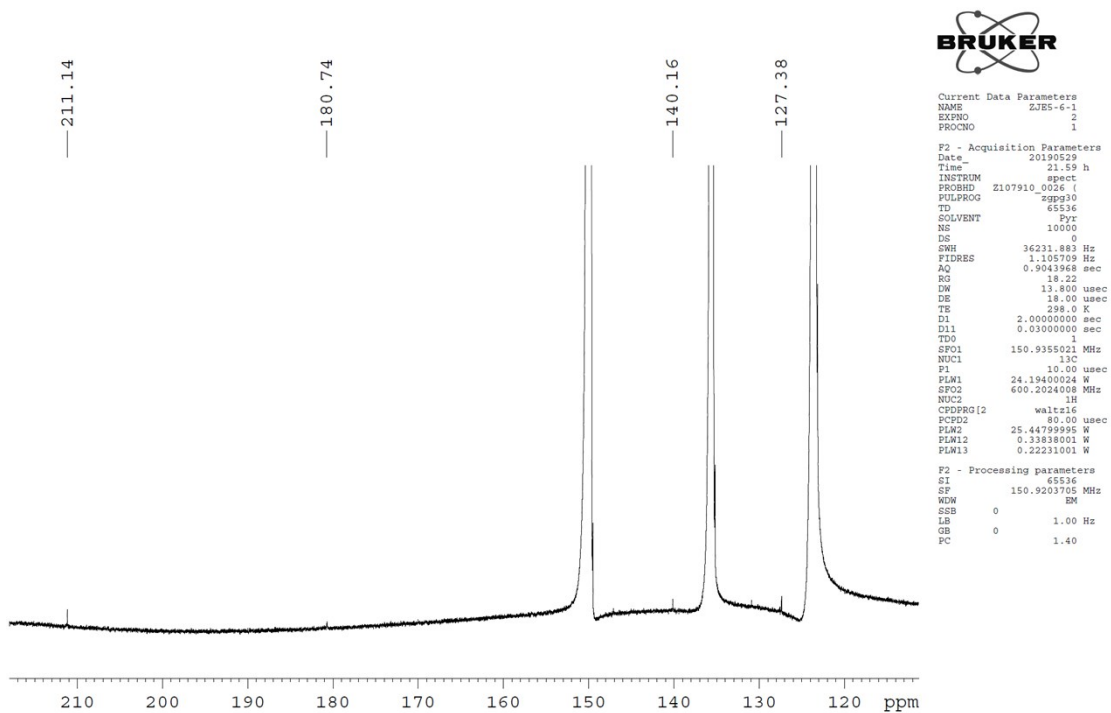
610
611
612

Fig. S84. ¹H NMR (600MHz, C₅D₅N) spectrum of compound 26



613
614
615

Fig. S85. ¹³C NMR (150MHz, C₅D₅N) spectrum-1 of compound 26

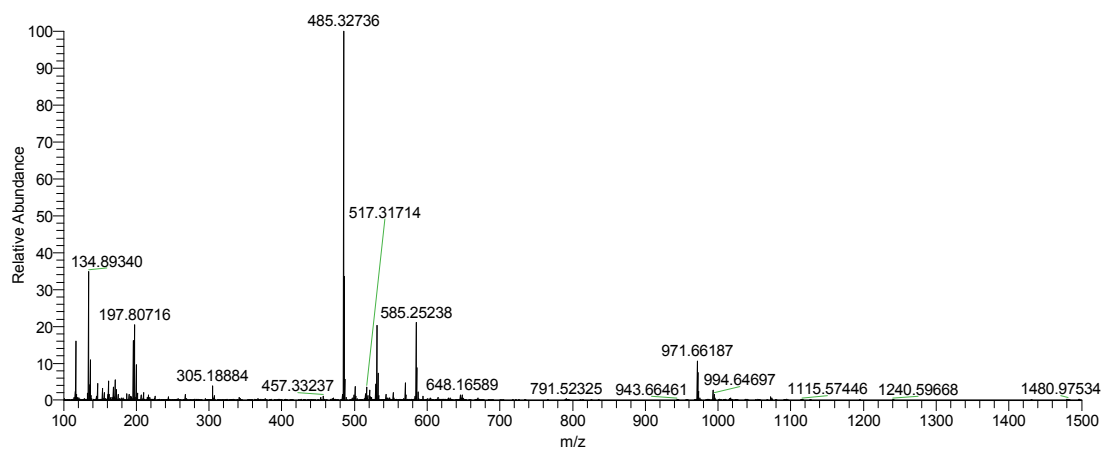


616

617

618

Fig. S86. ^{13}C NMR (150MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum-2 of compound **26**

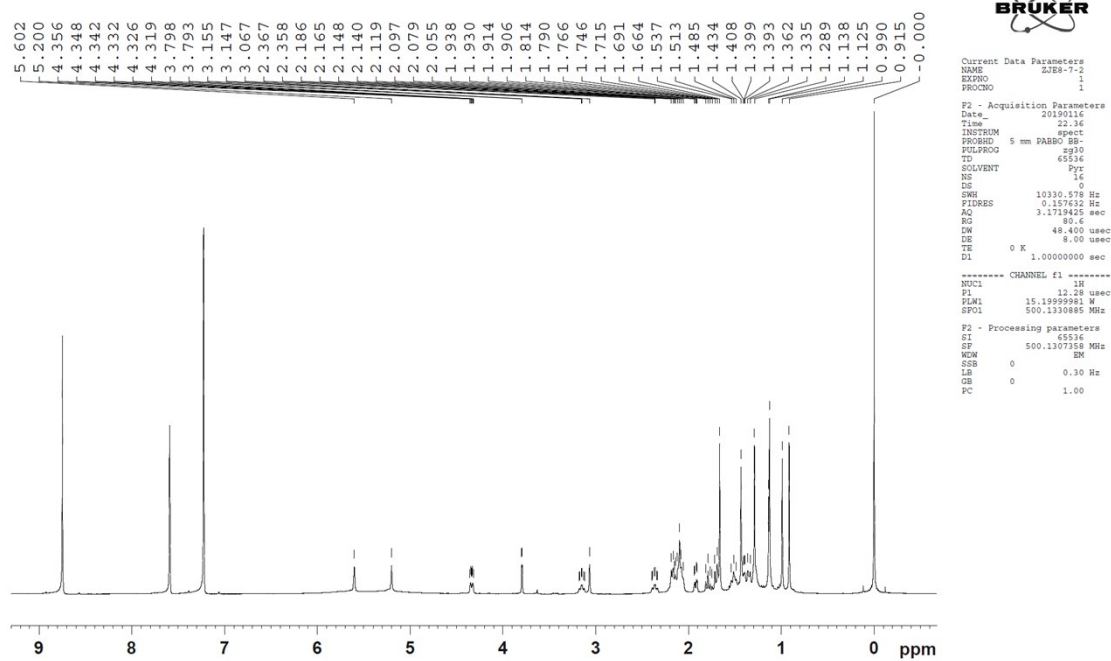


619

620

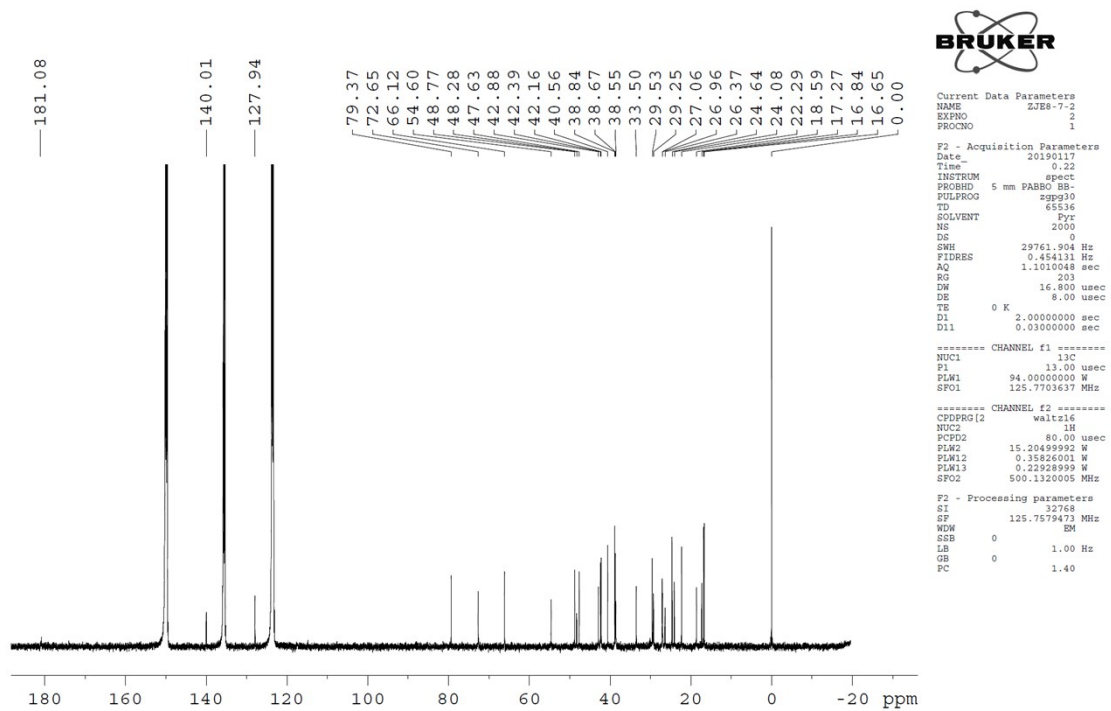
621

Fig. S87. The ESI-Q-Orbitrap MS spectrum of compound **26**



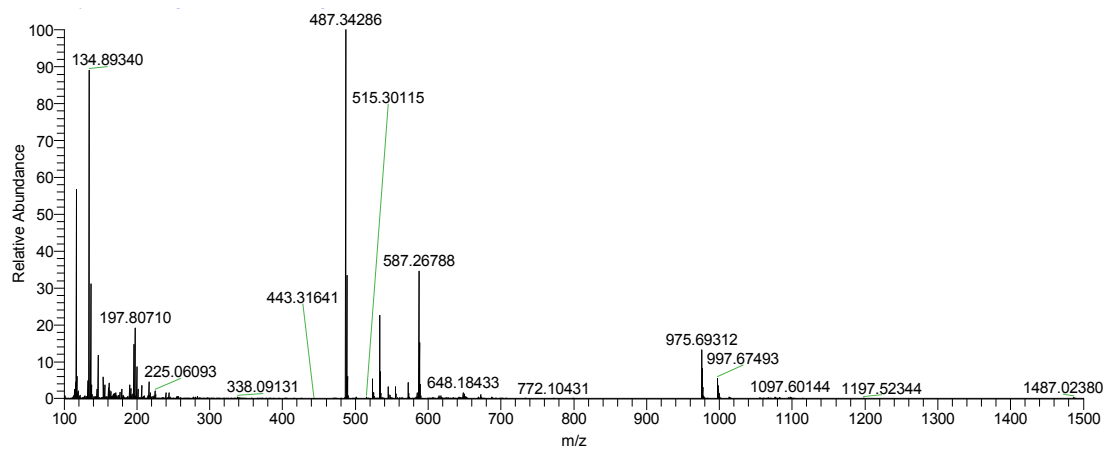
623
624
625

Fig. S88. ^1H NMR (500MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum of compound 27



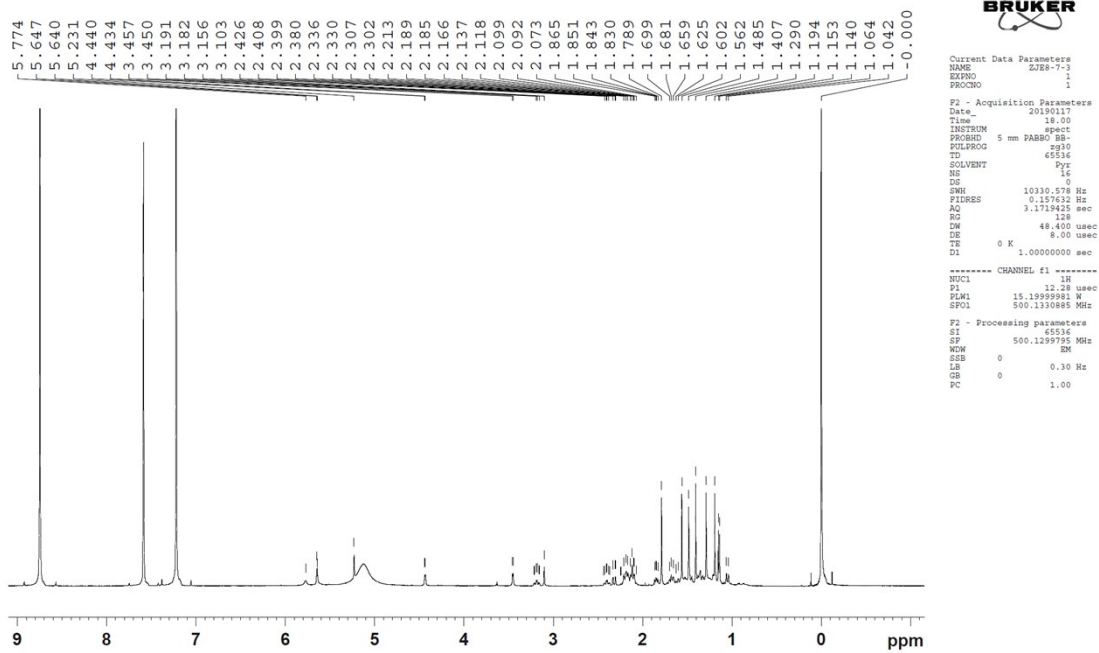
626
627
628

Fig. S89. ^{13}C NMR (125MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum of compound 27



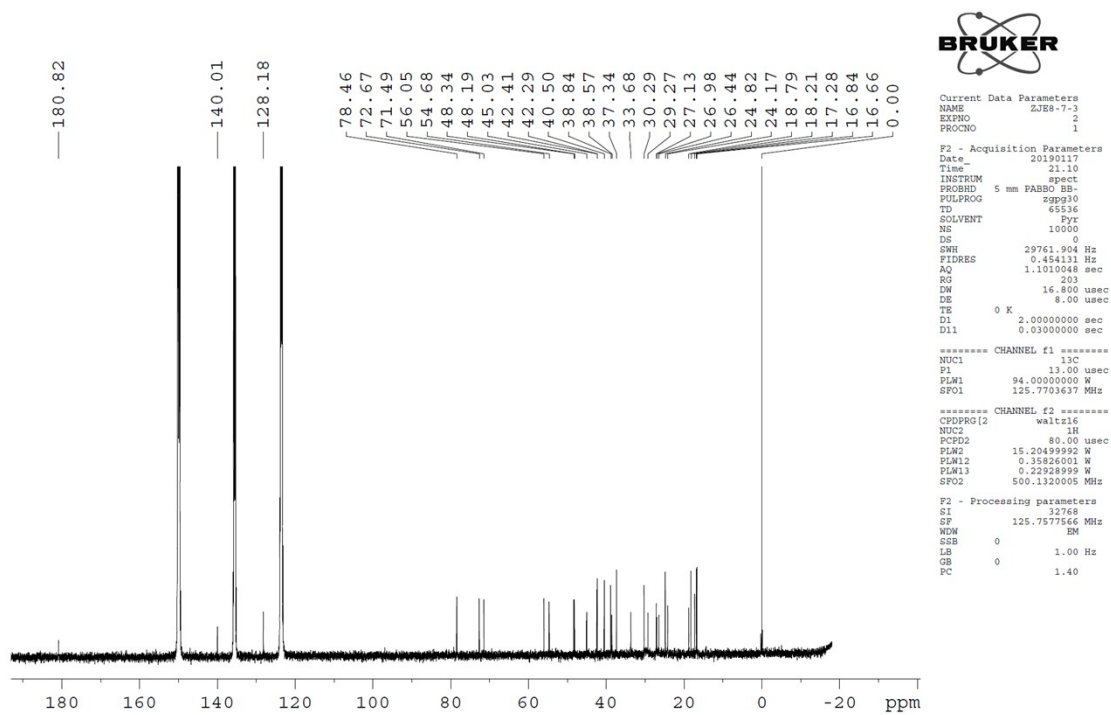
629
630
631

Fig. S90. The ESI-Q-Orbitrap MS spectrum of compound **27**



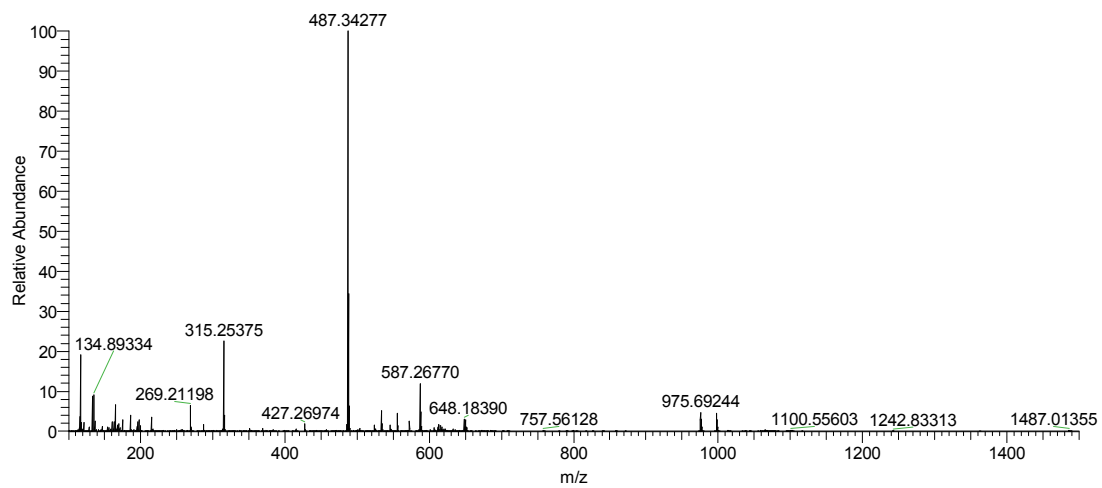
633
 634
 635

Fig. S91. ¹H NMR (500MHz, C₅D₅N) spectrum of compound 28



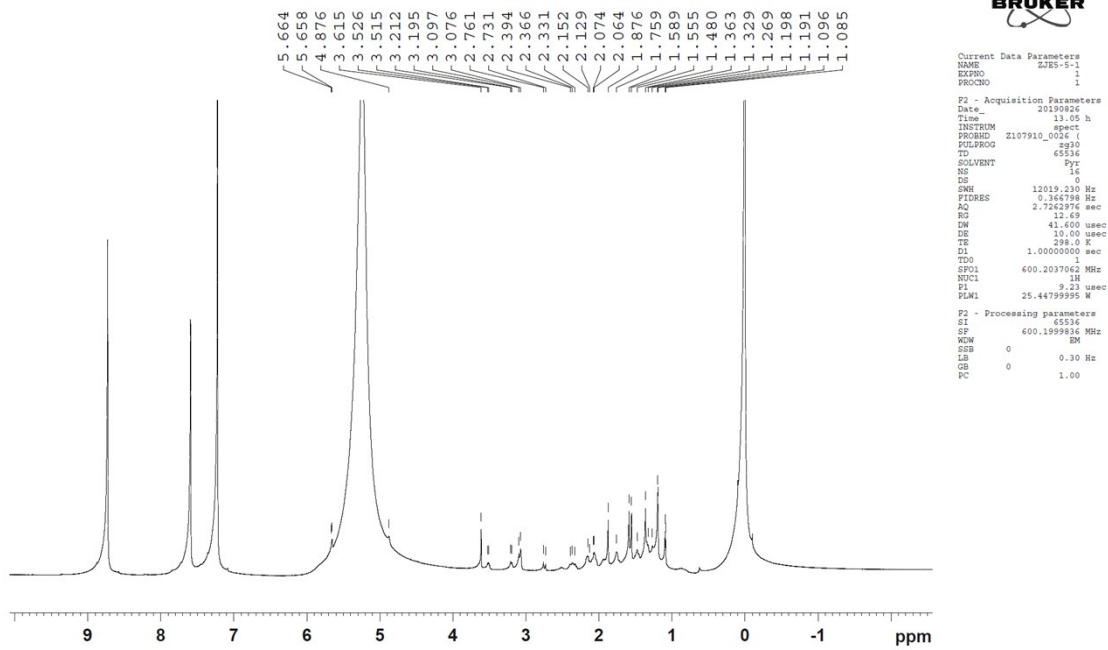
636
 637
 638

Fig. S92. ¹³C NMR (125MHz, C₅D₅N) spectrum of compound 28



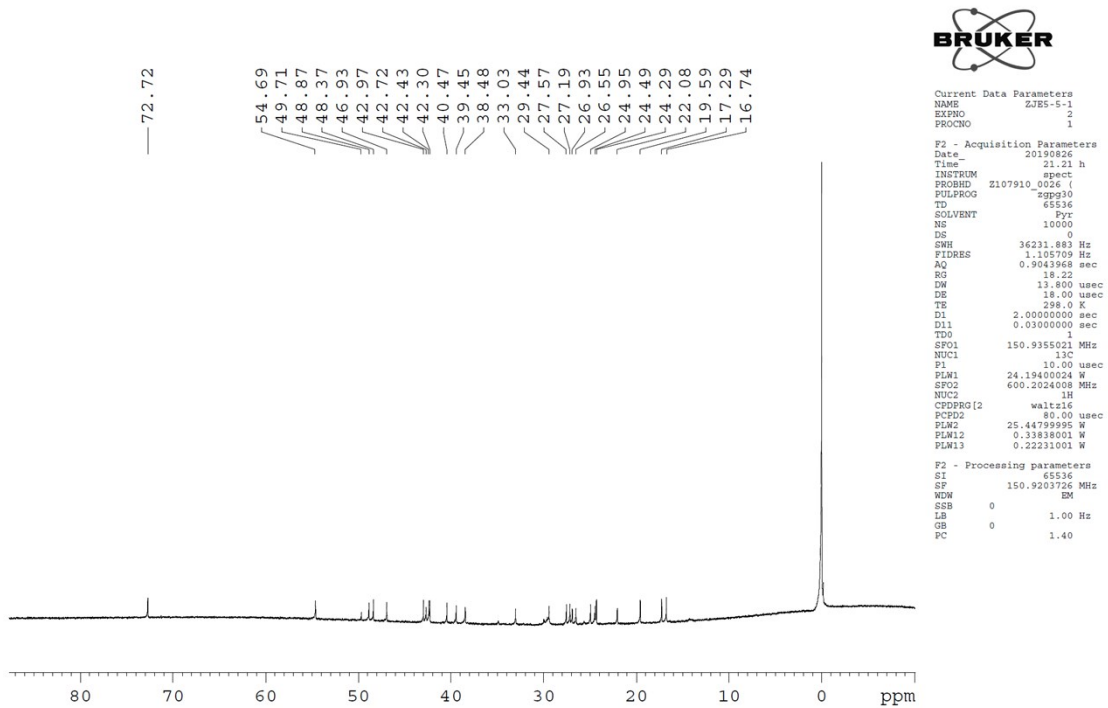
639
640
641

Fig. S93. The ESI-Q-Orbitrap MS spectrum of compound **28**



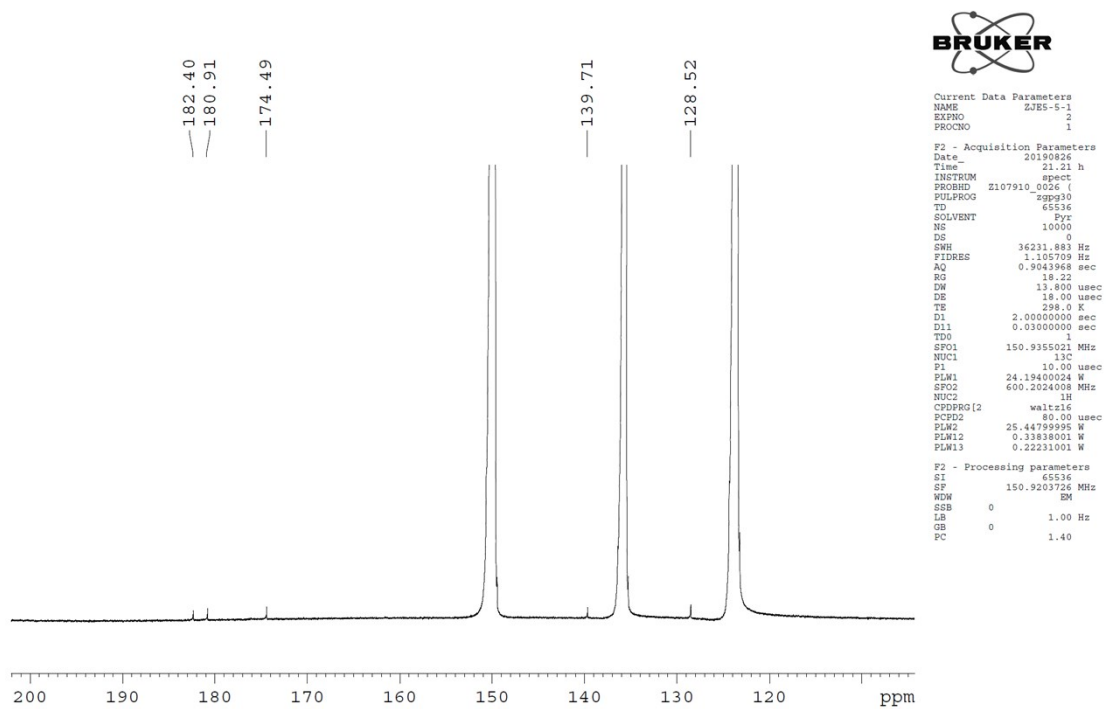
643
644
645

Fig. S94. ¹H NMR (600MHz, C₅D₅N) spectrum of compound 29



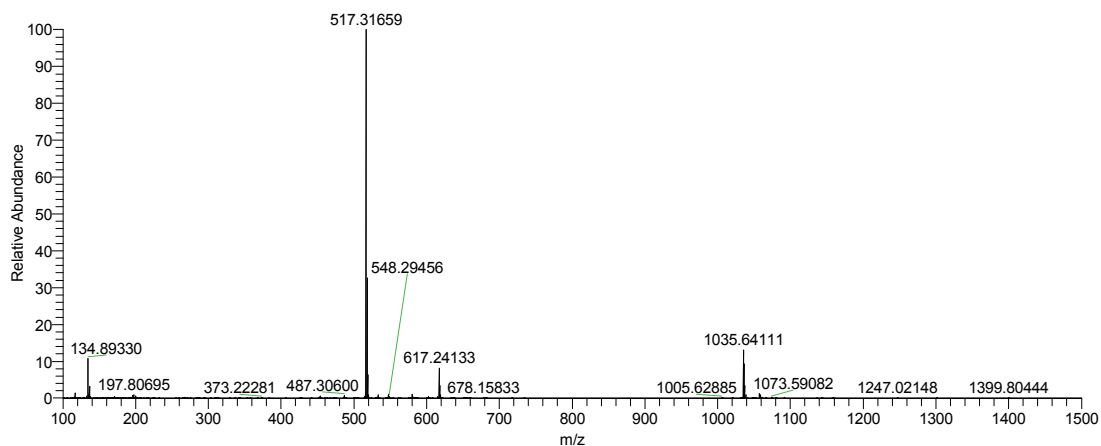
646
647
648

Fig. S95. ¹³C NMR (150MHz, C₅D₅N) spectrum-1 of compound 29



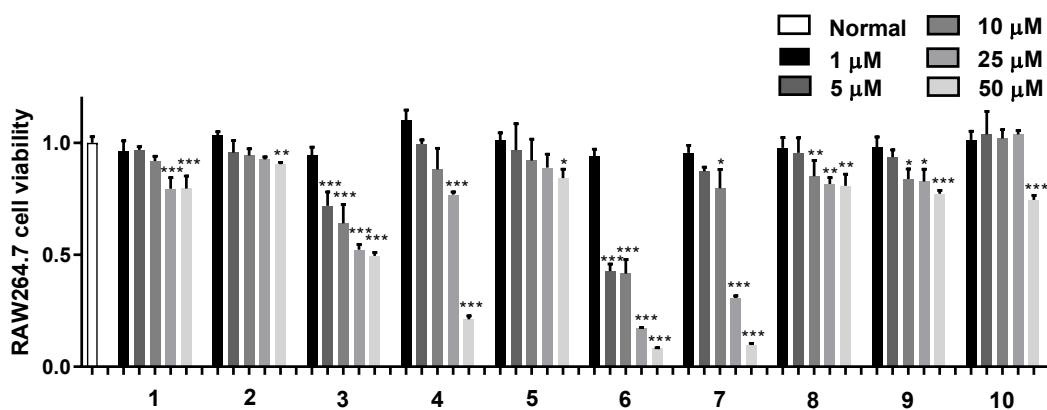
649
650
651

Fig. S96. ^{13}C NMR (150MHz, $\text{C}_5\text{D}_5\text{N}$) spectrum-2 of compound **29**

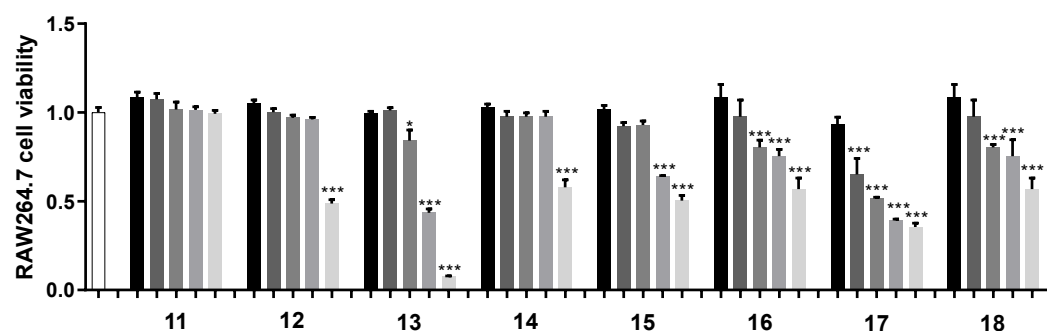


652
653

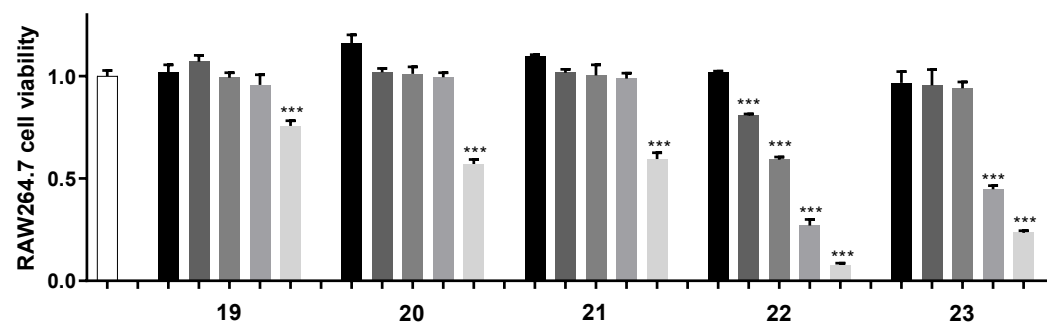
Fig. S97. The ESI-Q-Orbitrap MS spectrum of compound **29**



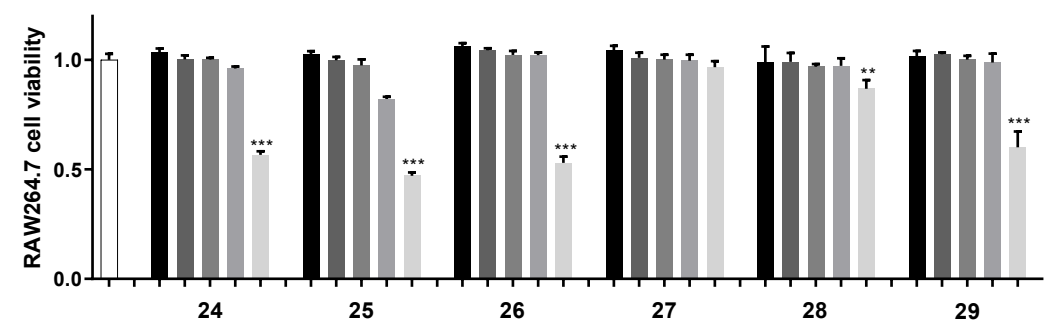
655



656



657



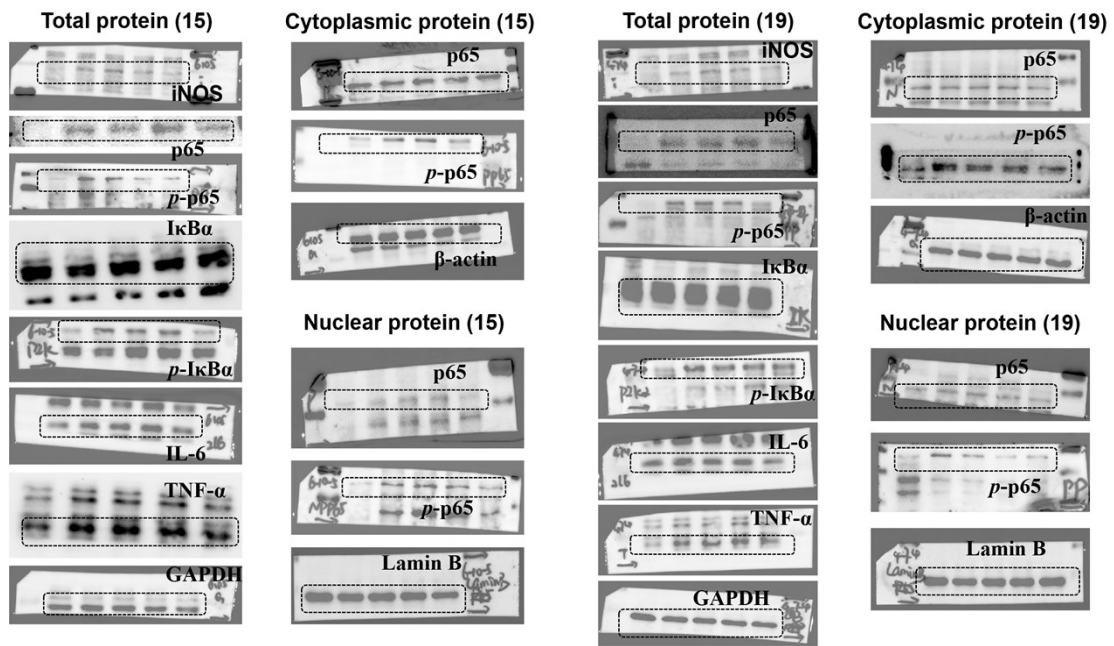
658

659

Fig. S98. The MTT assay compounds 1–29 at 1, 5, 10, 25 and 50 μM

660 N: normal group without tested samples. Values represent the mean \pm SD of six determinations.

661 ** $P < 0.01$, *** $P < 0.001$ (Differences between compound-treated group and normal group). $n = 6$.



663

664

Fig. S99. The raw data of Fig. 3

Tab. S1. ¹³C-NMR data for 2–11

No.	2 ^a	3 ^b	4 ^b	5 ^c	6 ^b	7 ^b	8 ^b	9 ^b	10 ^b	11 ^b
1	39.6	39.5	48.2	38.2	45.0	48.9	34.2	67.0	66.3	39.1
2	34.2	28.3	68.8	27.1	73.8	66.5	29.8	178.1	175.9	34.4
3	218.1	78.1	83.7	76.7	79.9	84.9	177.3	84.7	84.6	216.0
4	47.4	39.4	39.9	38.4	40.5	39.7	25.7	43.5	43.4	47.4
5	55.0	55.9	56.0	54.8	55.8	55.6	47.4	57.0	57.2	55.4
6	19.7	18.8	18.8	17.9	18.8	18.6	18.6	19.1	19.0	19.8
7	33.7	34.8	34.8	33.9	32.9	34.6	33.4	34.7	34.5	32.6
8	40.7	41.1	41.2	42.2	41.1	41.1	40.8	43.9	43.8	39.6
9	49.9	51.0	51.0	49.9	50.9	50.8	41.2	45.1	45.0	47.2
10	37.1	37.5	38.7	38.4	38.8	38.6	40.2	49.7	49.7	36.9
11	21.4	21.2	21.3	20.5	21.3	21.3	22.0	24.2	24.0	23.8
12	25.6	26.1	26.0	26.1	26.1	26.0	26.1	26.3	26.1	122.3
13	38.5	38.6	38.6	37.4	38.6	38.5	38.7	39.1	39.0	144.9
14	42.5	42.8	42.9	40.2	42.9	42.9	43.3	42.1	42.1	42.2
15	29.8	30.3	30.2	29.2	30.2	30.2	30.3	30.5	30.5	28.3
16	32.3	32.9	32.9	31.7	32.9	32.8	32.9	33.0	32.9	23.7
17	56.4	56.6	56.6	55.4	56.6	56.6	56.8	56.6	56.7	46.7
18	49.3	49.8	49.8	48.8	49.8	49.7	49.7	49.7	49.7	42.1
19	46.9	47.8	47.8	41.9	47.8	47.8	47.8	47.6	47.7	46.4
20	150.6	151.3	151.3	155.5	151.4	151.3	151.5	151.2	151.2	31.0
21	30.7	31.2	31.2	28.6	31.2	31.2	31.3	31.3	31.3	34.2
22	37.0	37.6	37.6	36.2	37.7	37.6	37.6	37.6	37.6	33.2
23	26.7	28.7	29.2	28.0	29.1	28.9	24.9	31.5	31.5	26.6
24	21.0	16.4	17.4	15.7	16.3	18.0	19.1	20.4	20.2	21.6
25	15.9	16.4	17.7	15.9	17.4	17.6	20.0	18.8	18.6	14.9
26	16.0	16.4	16.5	15.9	17.4	16.4	16.4	17.0	17.0	17.2
27	14.6	14.9	14.9	14.3	14.9	14.9	14.8	15.1	15.0	26.0
28	180.3	179.0	179.1	177.2	179.0	179.0	179.4	178.9	179.0	180.2
29	19.4	19.5	19.5	62.8	19.4	19.4	19.5	19.6	19.5	33.3
30	109.6	110.0	109.9	105.3	110.0	110.0	110.0	109.8	109.9	23.7
2-OCH ₃									51.1	
1'					126.2	126.7				
2'					130.6	133.8				
3'					116.9	115.9				
4'					161.4	160.5				
5'					116.9	115.9				
6'					130.6	133.8				
7'					144.7	143.6				
8'					116.0	117.1				
9'					167.5	167.2				

667 ^a CDCl₃; ^b C₅D₅N; ^c DMSO-*d*₆; ^d CD₃OD

Tab. S2. ¹³C-NMR data for 12–20

No.	12 ^b	13 ^b	14 ^d	15 ^c	16 ^c	17 ^b	18 ^b	19 ^b	20 ^b
1	39.0	47.7	48.5	43.4	43.4	48.3	34.1	39.3	39.1
2	28.1	68.6	69.2	71.8	71.8	66.4	29.8	34.3	28.1
3	78.1	83.8	84.2	78.2	78.2	85.0	177.3	216.1	78.1
4	39.4	39.8	40.6	40.7	40.9	39.8	25.3	47.1	39.4
5	55.8	55.9	56.2	54.2	54.2	55.5	47.9	55.3	55.8
6	18.8	18.8	18.7	18.0	18.0	18.7	18.5	19.8	18.8
7	33.2	33.2	34.0	32.1	32.1	33.0	32.2	32.9	33.6
8	39.8	39.8	45.1	39.2	38.8	39.8	39.6	39.8	40.0
9	48.2	48.1	63.0	46.7	46.7	48.0	38.4	47.3	48.1
10	37.4	38.5	39.4	37.7	37.7	38.4	40.2	36.8	37.5
11	23.9	23.9	202.7	23.2	23.2	23.9	24.1	23.7	23.7
12	122.6	122.4	128.3	121.2	121.2	122.3	122.7	125.4	125.7
13	144.9	144.8	173.1	143.9	143.9	145.0	144.8	139.3	140.1
14	42.2	42.2	46.5	41.3	41.3	42.2	42.7	42.5	42.5
15	28.4	28.3	28.9	27.1	27.1	28.3	28.4	28.6	28.7
16	23.7	23.7	24.0	22.8	22.8	23.7	23.8	24.9	24.9
17	46.7	46.6	47.3	45.6	45.6	46.7	46.8	48.1	48.1
18	42.1	42.0	43.5	41.3	40.9	42.0	42.1	53.6	53.6
19	46.5	46.5	45.7	45.3	45.3	46.5	46.5	39.5	39.5
20	31.0	30.9	31.7	30.3	30.0	31.0	31.0	39.4	39.4
21	34.3	34.2	34.8	33.2	33.2	34.3	34.3	31.1	31.1
22	33.2	33.2	33.0	32.0	32.1	33.2	33.2	37.4	37.3
23	28.8	29.3	29.3	28.5	28.4	29.0	24.9	26.7	28.8
24	16.6	17.6	17.5	16.9	16.7	18.3	19.1	21.6	16.6
25	15.6	16.8	18.0	16.0	16.0	16.8	19.5	15.1	15.7
26	17.5	17.5	19.9	16.7	16.9	17.4	17.6	17.3	17.5
27	26.2	26.2	24.0	25.5	25.5	26.2	26.0	23.7	23.9
28	180.3	180.2	181.4	178.7	179.7	180.5	180.5	179.8	180.0
29	33.3	33.3	33.3	32.7	32.7	33.3	33.3	17.5	17.6
30	23.8	23.8	23.8	23.3	23.3	23.8	23.8	21.4	21.4
1'				125.1	125.8	126.2			
2'				130.0	132.5	130.6			
3'				115.7	114.7	116.8			
4'				159.6	159.2	161.4			
5'				115.7	114.7	116.8			
6'				130.0	132.5	130.6			
7'				144.0	142.3	144.8			
8'				114.9	116.2	116.0			
9'				166.3	166.3	167.9			

Tab. S3. ¹³C-NMR data for 21–29

No.	21 ^b	22 ^b	23 ^b	24 ^b	25 ^b	26 ^b	27 ^b	28 ^b	29 ^b
1	47.9	48.6	34.3	39.2	39.0	53.7	42.9	45.0	42.4
2	68.6	66.4	29.9	34.4	28.2	211.2	66.1	71.5	174.5
3	83.8	85.1	177.3	216.5	78.2	83.5	79.4	78.5	182.4
4	39.8	39.8	25.4	47.5	39.4	45.8	38.8	38.8	46.9
5	55.9	55.6	47.9	55.5	55.9	54.9	48.8	56.1	48.9
6	18.8	18.7	18.6	19.9	19.0	19.2	18.6	18.8	22.1
7	33.5	33.4	31.2	33.0	33.7	33.2	33.5	33.7	33.0
8	40.0	40.0	39.8	40.2	40.4	42.3	40.6	40.5	40.5
9	48.1	48.0	38.2	46.9	47.8	47.4	47.6	48.2	39.5
10	38.4	38.3	40.1	36.9	37.4	40.7	38.7	37.3	48.4
11	23.9	23.7	24.1	24.0	24.1	23.9	24.1	24.2	24.5
12	125.5	125.4	125.8	127.8	128.0	127.4	127.9	128.2	128.5
13	139.3	139.6	139.3	140.0	140.1	140.2	140.0	140.0	139.7
14	42.5	42.6	43.1	42.2	42.2	43.7	42.2	42.3	42.7
15	28.6	28.7	28.7	29.3	29.4	29.5	29.3	29.3	29.4
16	24.9	24.9	25.0	26.4	26.5	26.4	26.4	26.4	26.6
17	48.0	48.1	48.1	48.3	48.4	48.3	48.3	48.3	48.4
18	53.5	53.6	53.7	54.7	54.7	54.6	54.6	54.7	54.7
19	39.5	39.5	39.6	72.7	72.7	72.7	72.7	72.7	72.7
20	39.4	39.4	39.4	42.4	42.4	42.4	42.4	42.4	42.3
21	31.1	31.1	32.5	26.9	27.0	27.0	27.0	27.0	26.9
22	37.4	37.5	37.5	38.5	38.6	38.5	38.6	38.6	38.5
23	29.4	29.0	24.9	26.6	28.8	29.3	29.5	30.3	27.6
24	17.7	18.3	19.7	21.6	16.6	16.8	22.3	18.2	25.0
25	17.0	16.8	19.7	15.0	15.6	16.4	16.7	16.7	19.6
26	17.5	17.4	17.7	17.0	17.3	17.3	17.3	17.3	17.3
27	23.7	24.0	23.8	24.5	24.7	24.6	24.6	24.8	24.3
28	179.9	180.3	180.2	180.8	180.9	180.7	181.1	180.8	180.9
29	17.5	17.5	17.7	27.1	27.2	27.1	27.1	27.1	27.2
30	21.4	21.4	21.4	16.8	16.8	16.8	16.8	16.8	16.7
1'		126.3							
2'		130.6							
3'		116.8							
4'		161.4							
5'		116.8							
6'		130.6							
7'		144.8							
8'		116.1							
9'		167.9							

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Tab. S4. Comparison ^1H and ^{13}C NMR chemical shifts of maslinic acid, augustic acid, bredemolic acid and 3-*epi*-maslinic acid

	Maslinic acid (2α3β)	3-<i>epi</i>-Maslinic acid (2α3α)	Bredemolic acid (2β3α)	Augustic acid (2β3β)
$\delta_{\text{H-2}}$	4.11	4.21	4.36	4.41
$\delta_{\text{H-3}}$	3.41	3.77	4.00	3.44
$\Delta\delta_{\text{H2-H3}}$	0.7	0.56	0.36	0.97
$J_{\text{H2,3}}$	9.4	2.6	7.5	4.0
$\delta_{\text{C-2}}$	69.0	66.5	71.1	71.8
$\delta_{\text{C-3}}$	84.3	79.7	78.7	78.7
$\Delta\delta_{\text{C3-C2}}$	15.3	13.2	7.6	6.9

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