

Supplementary material

for

# ***Pulicaria dysenterica* (L.) Bernh. — Rightfully Earned Name? Identification and Biological Activity of New 3-Methoxycuminyll Esters from *P. dysenterica* Essential Oil**

Niko S. Radulović <sup>1,\*</sup>, Marko Z. Mladenović <sup>1</sup>, Dušan R. Vukićević <sup>2</sup>, Nikola M. Stojanović <sup>3</sup>, Pavle J. Randjelović <sup>3</sup>, Zorica Z. Stojanović-Radić <sup>4</sup> and Fabio Boylan <sup>5</sup>

<sup>1</sup> Department of Chemistry, Faculty of Sciences and Mathematics, University of Nis, Višegradska 33, 18000 Nis, Serbia

<sup>2</sup> Faculty of Medicine, University of Kragujevac, Svetozara Markovića 69, 34000 Kragujevac, Serbia

<sup>3</sup> Department of Physiology, Faculty of Medicine, University of Nis, Zorana Đindića 81, 18000 Nis, Serbia

<sup>4</sup> Department of Biology and Ecology, Faculty of Sciences and Mathematics, University of Nis, Višegradska 33, 18000 Nis, Serbia

<sup>5</sup> School of Pharmacy and Pharmaceutical Sciences, Panoz Institute, Trinity College, Westland Row, 2 Dublin, Ireland

\* Correspondence: nikoradulovic@yahoo.com; Tel.: +381-18-533-015; Fax: +381-18-533-014

## **Content:**

**Figure S1.** Mass spectrum of 3-methoxycuminyll isobutanoate (7).

**Figure S2.** <sup>1</sup>H NMR spectrum of 3-methoxycuminyll isobutanoate (7).

**Figure S3.** <sup>13</sup>C NMR spectrum of 3-methoxycuminyll isobutanoate (7).

**Figure S4.** <sup>13</sup>C NMR spectrum (without heteronuclear decoupling) of 3-methoxycuminyll isobutanoate (7).

**Figure S5.** Distortionless enhancement by polarization transfer spectrum (DEPT90) of 3-methoxycuminyll isobutanoate (7).

**Figure S6.** Distortionless enhancement by polarization transfer spectrum (DEPT135) of 3-methoxycuminyll isobutanoate (7).

**Figure S7.** Gradient <sup>1</sup>H–<sup>1</sup>H COSY spectrum of 3-methoxycuminyll isobutanoate (7).

**Figure S8.** Gradient HSQC spectrum of 3-methoxycuminyll isobutanoate (7).

**Figure S9.** Gradient HMBC spectrum of 3-methoxycuminyll isobutanoate (7).

**Figure S10.** Mass spectrum of 3-methoxycuminyll butanoate (8).

**Figure S11.** <sup>1</sup>H NMR spectrum of 3-methoxycuminyll butanoate (8).

**Figure S12.** <sup>13</sup>C NMR spectrum of 3-methoxycuminyll butanoate (8).

**Figure S13.** Mass spectrum of 3-methoxycuminyll 2-methylbutanoate (9).

**Figure S14.** <sup>1</sup>H NMR spectrum of 3-methoxycuminyll 2-methylbutanoate (9).

**Figure S15.** <sup>13</sup>C NMR spectrum of 3-methoxycuminyll 2-methylbutanoate (9).

**Figure S16.**  $^{13}\text{C}$  NMR spectrum (without heteronuclear decoupling) of 3-methoxycuminy 2-methylbutanoate (**9**).

**Figure S17.** Distortionless enhancement by polarization transfer spectrum (DEPT90) of 3-methoxycuminy 2-methylbutanoate (**9**).

**Figure S18.** Distortionless enhancement by polarization transfer spectrum (DEPT135) of 3-methoxycuminy 2-methylbutanoate (**9**).

**Figure S19.** Gradient  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of 3-methoxycuminy 2-methylbutanoate (**9**).

**Figure S20.** Gradient HSQC spectrum of 3-methoxycuminy 2-methylbutanoate (**9**).

**Figure S21.** Gradient HMBC spectrum of 3-methoxycuminy 2-methylbutanoate (**9**).

**Figure S22.** Mass spectrum of 3-methoxycuminy 3-methylbutanoate (**10**).

**Figure S23.**  $^1\text{H}$  NMR spectrum of 3-methoxycuminy 3-methylbutanoate (**10**).

**Figure S24.**  $^{13}\text{C}$  NMR spectrum of 3-methoxycuminy 3-methylbutanoate (**10**).

**Figure S25.**  $^{13}\text{C}$  NMR spectrum (without heteronuclear decoupling) of 3-methoxycuminy 3-methylbutanoate (**10**).

**Figure S26.** Distortionless enhancement by polarization transfer spectrum (DEPT90) of 3-methoxycuminy 3-methylbutanoate (**10**).

**Figure S27.** Distortionless enhancement by polarization transfer spectrum (DEPT135) of 3-methoxycuminy 3-methylbutanoate (**10**).

**Figure S28.** Gradient  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of 3-methoxycuminy 3-methylbutanoate (**10**).

**Figure S29.** Gradient HSQC spectrum of 3-methoxycuminy 3-methylbutanoate (**10**).

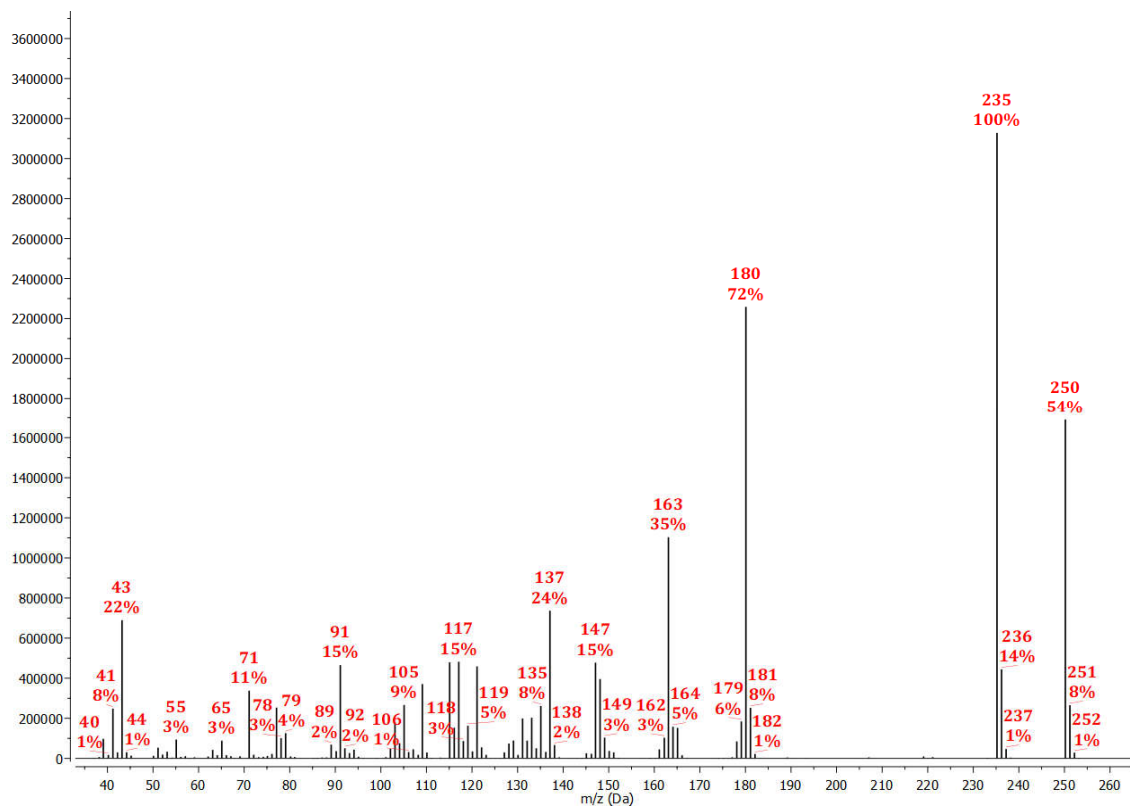
**Figure S30.** Gradient HMBC spectrum of 3-methoxycuminy 3-methylbutanoate (**10**).

**Figure S31.** Mass spectrum of 3-methoxycuminy pentanoate (**11**).

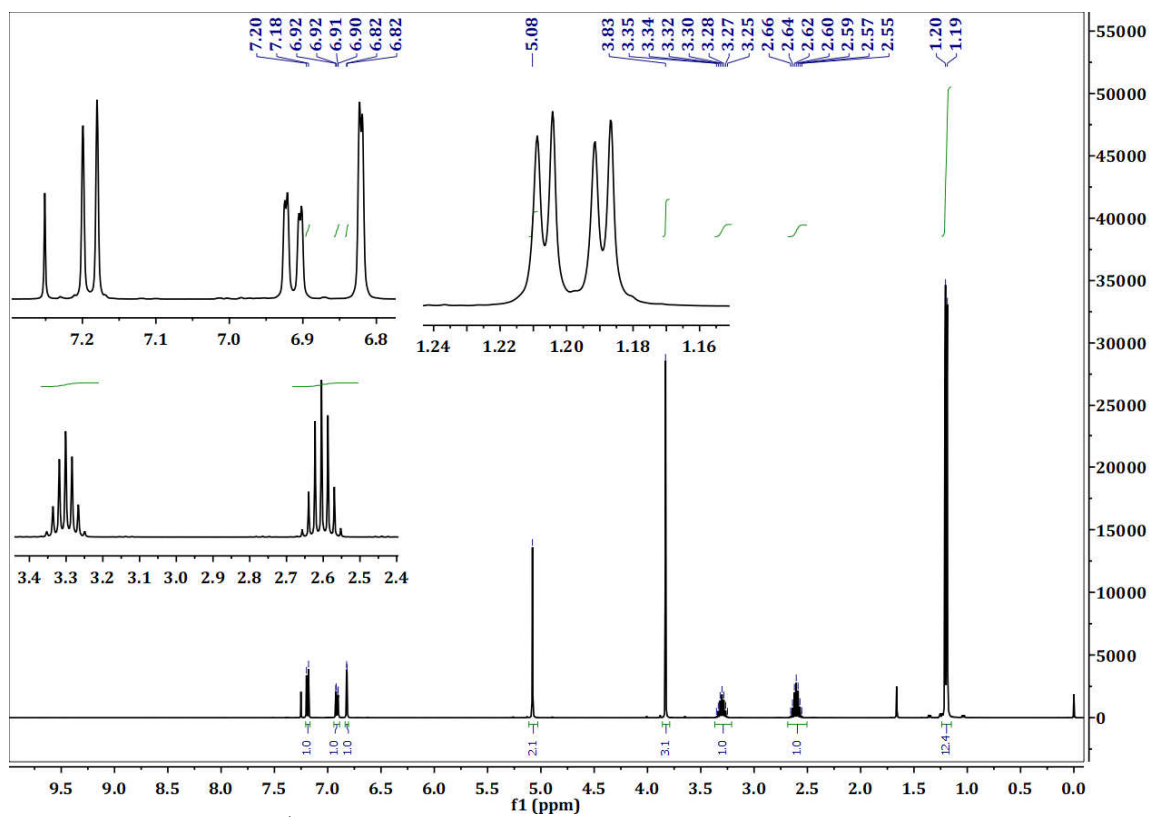
**Figure S32.**  $^1\text{H}$  NMR spectrum of 3-methoxycuminy pentanoate (**11**).

**Figure S33.**  $^{13}\text{C}$  NMR spectrum of 3-methoxycuminy pentanoate (**11**).

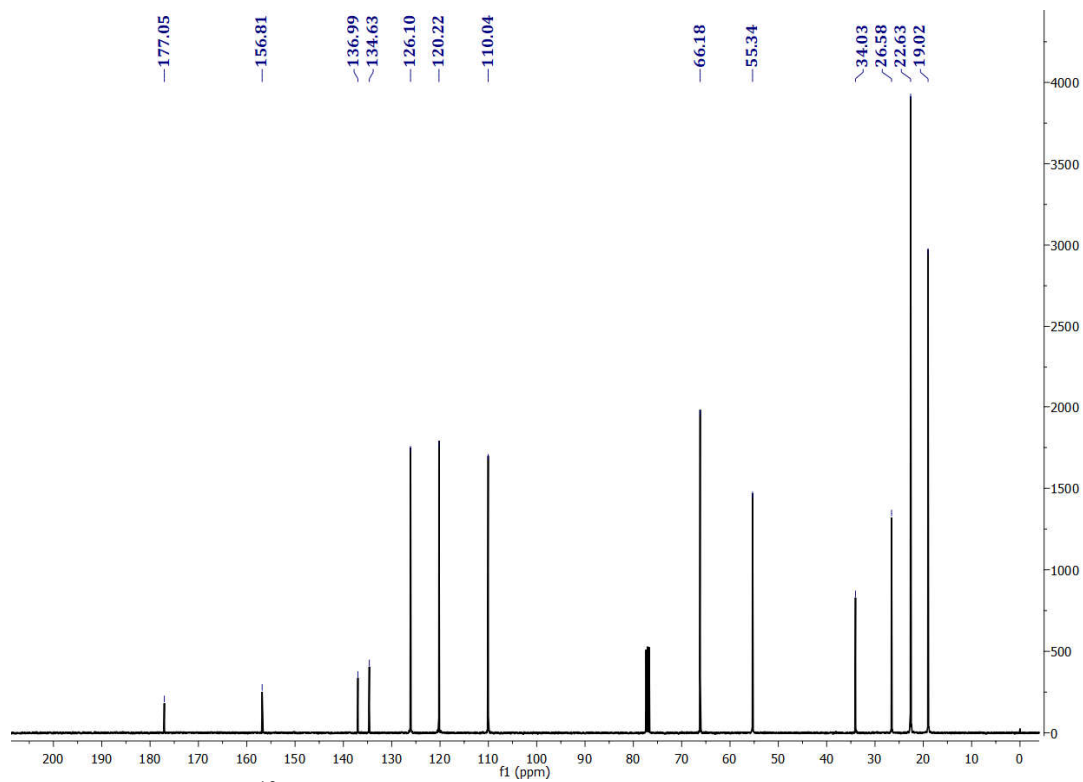
**Figure S34.** Spin simulation of the  $^1\text{H}$  NMR signals for the protons at position 13 and 14 (lower) and comparison with the experimental ones (upper) for 3-methoxycuminy 2-methylbutanoate (**9**).



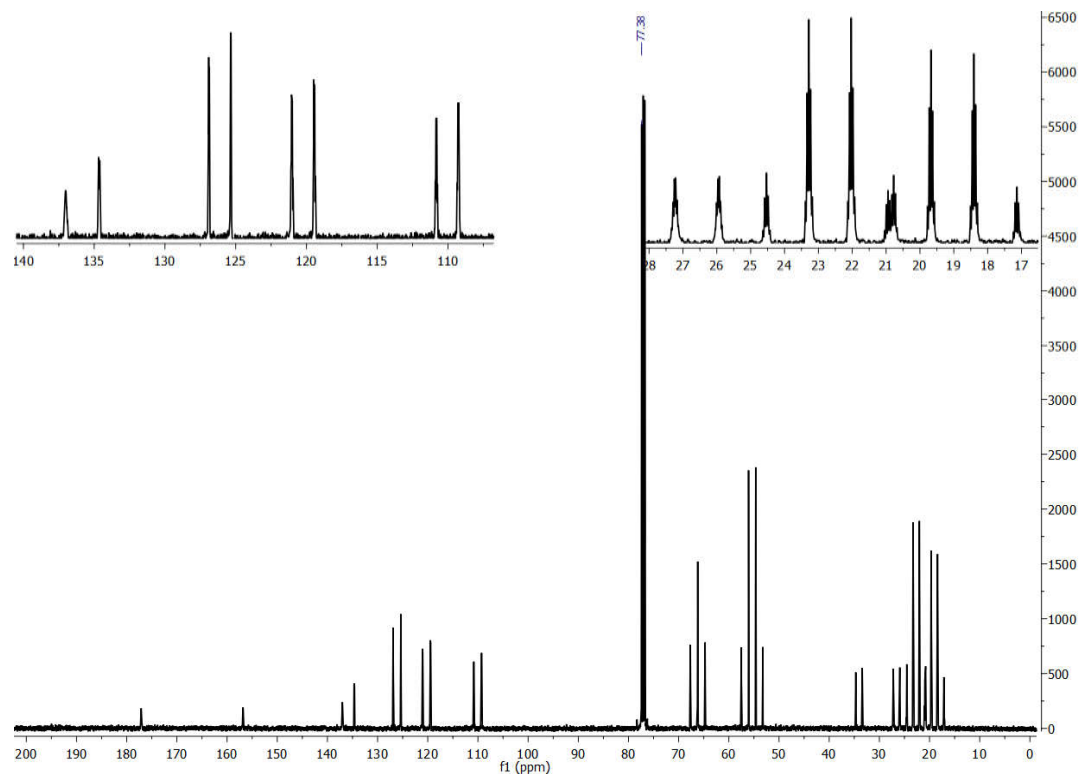
**Figure S1.** Mass spectrum of 3-methoxycuminyll isobutanoate (7).



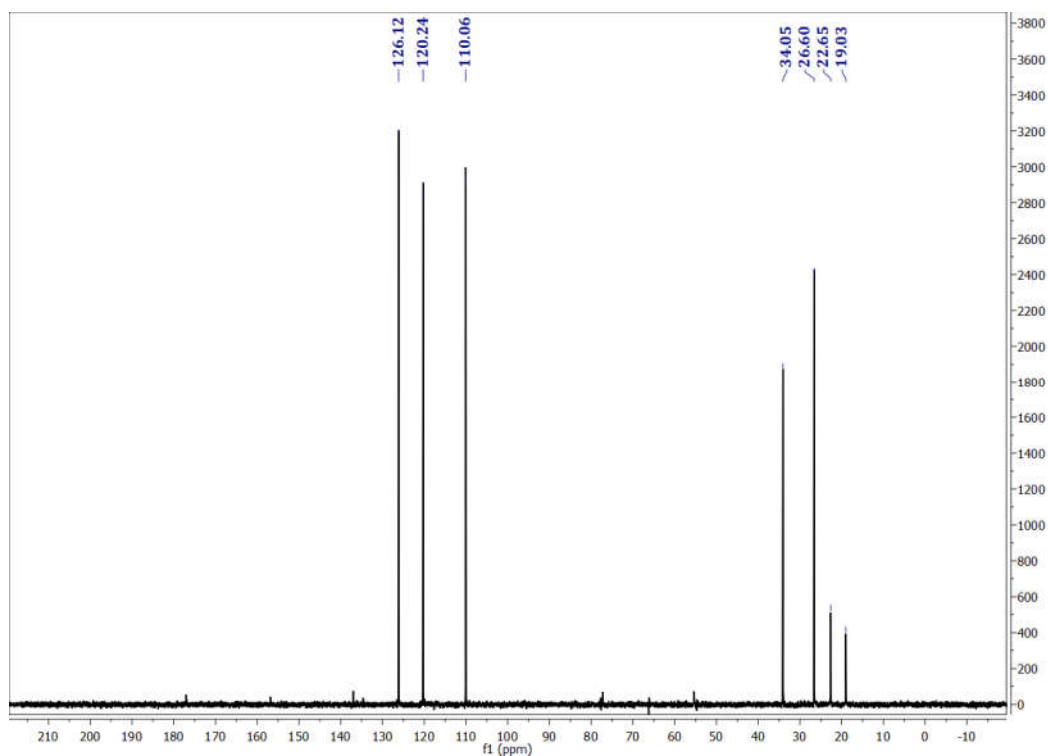
**Figure S2.**  $^1\text{H}$  NMR spectrum of 3-methoxycuminyll isobutanoate (7).



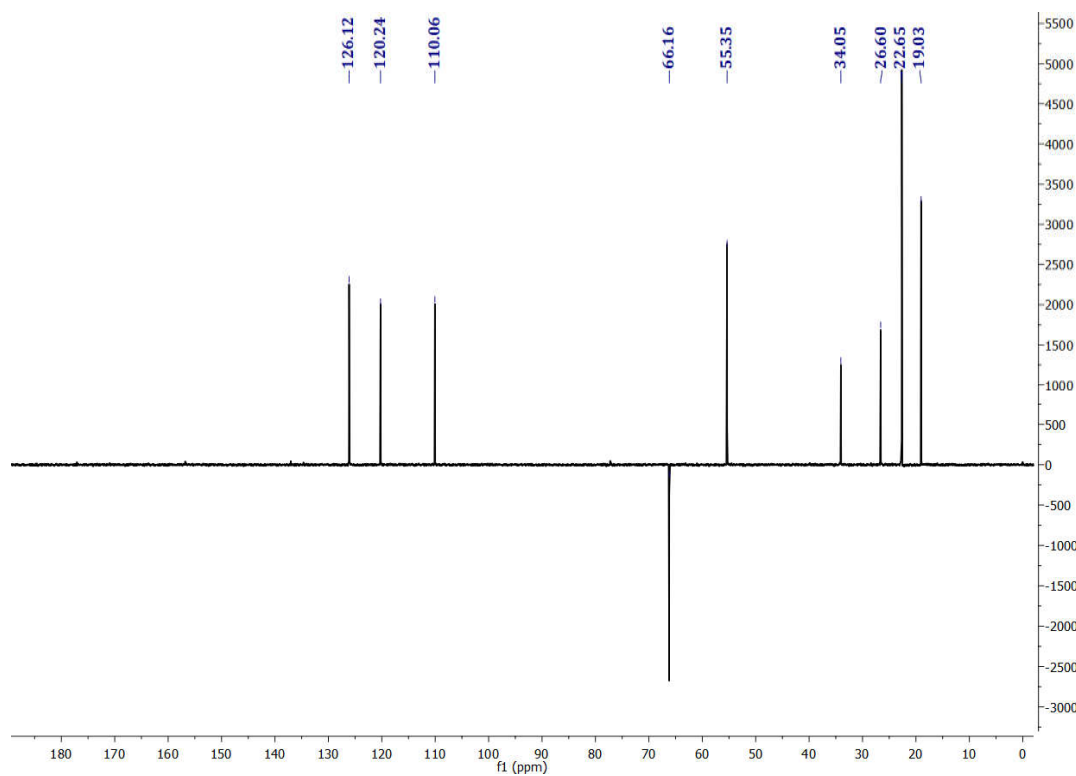
**Figure S3.**  $^{13}\text{C}$  NMR spectrum of 3-methoxycuminyll isobutanoate (7).



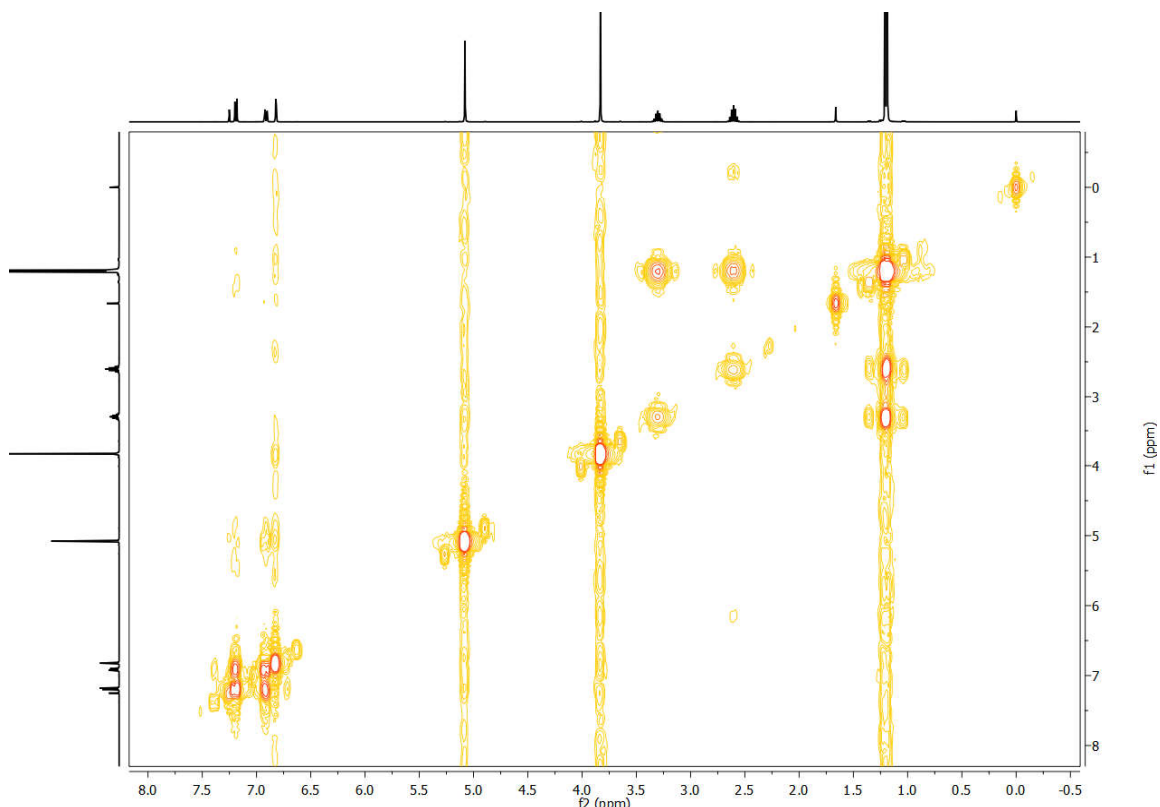
**Figure S4.**  $^{13}\text{C}$  NMR spectrum (without heteronuclear decoupling) of 3-methoxycuminyll isobutanoate (7).



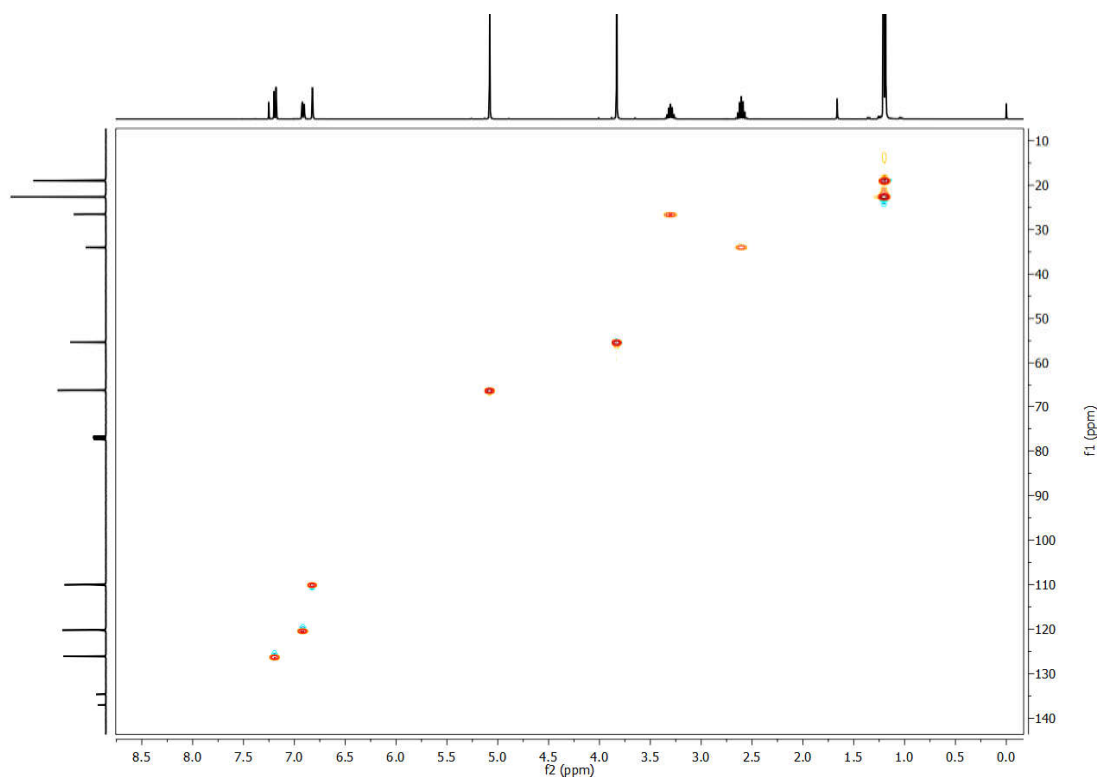
**Figure S5.** Distortionless enhancement by polarization transfer spectrum (DEPT90) of 3-methoxycumyl isobutanoate (**7**).



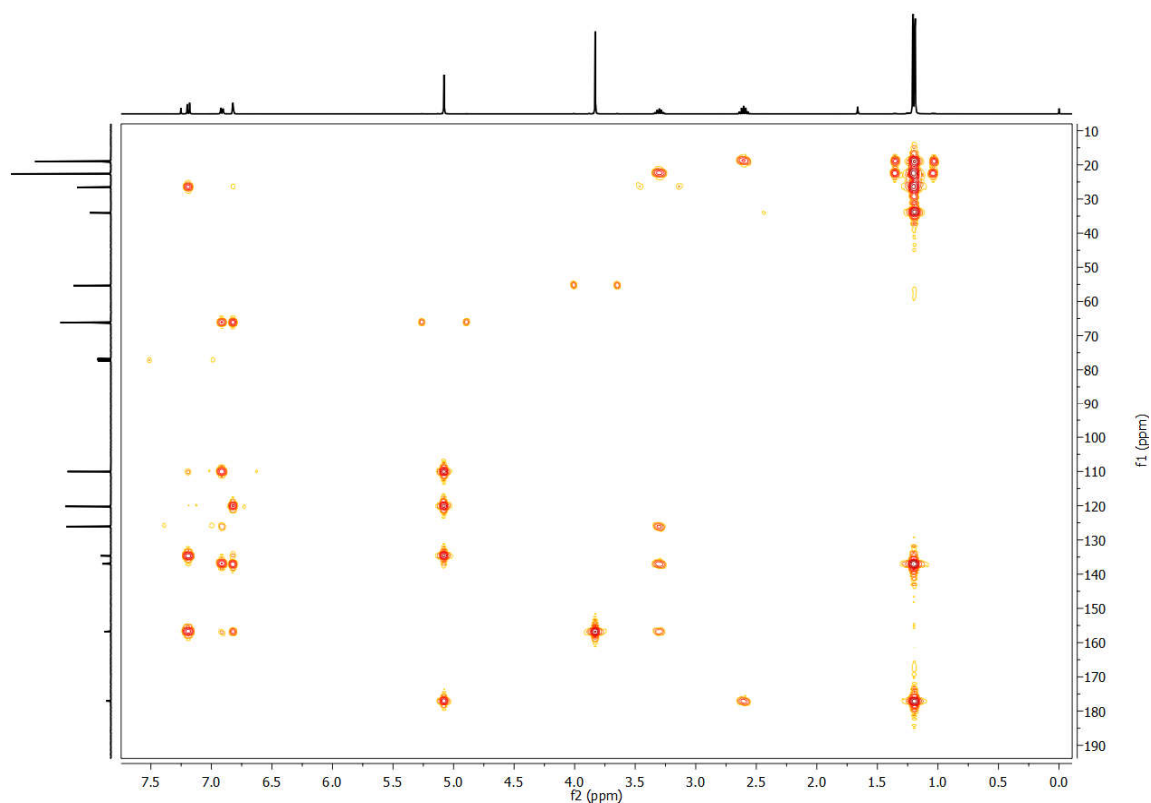
**Figure S6.** Distortionless enhancement by polarization transfer spectrum (DEPT135) of 3-methoxycumyl isobutanoate (**7**).



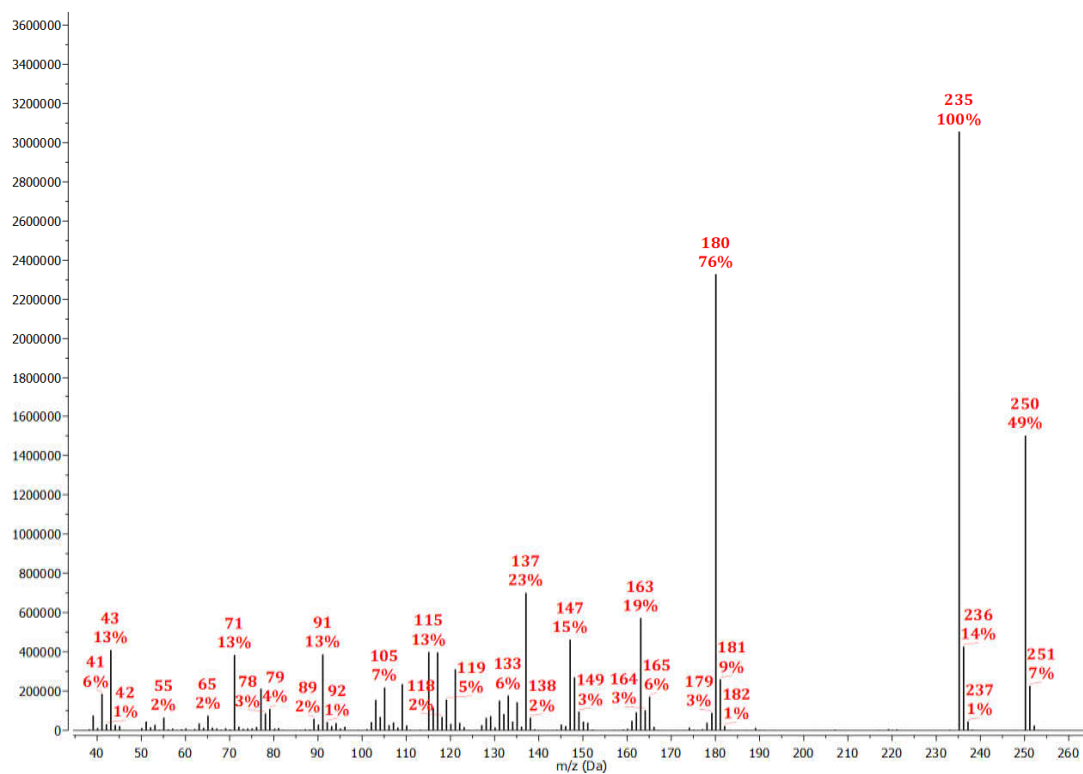
**Figure S7.** Gradient  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of 3-methoxycuminyll isobutanoate (**7**).



**Figure S8.** Gradient HSQC spectrum of 3-methoxycuminyll isobutanoate (**7**).



**Figure S9.** Gradient HMBC spectrum of 3-methoxycuminy isobutanoate (7).



**Figure S10.** Mass spectrum of 3-methoxycuminy butanoate (8).

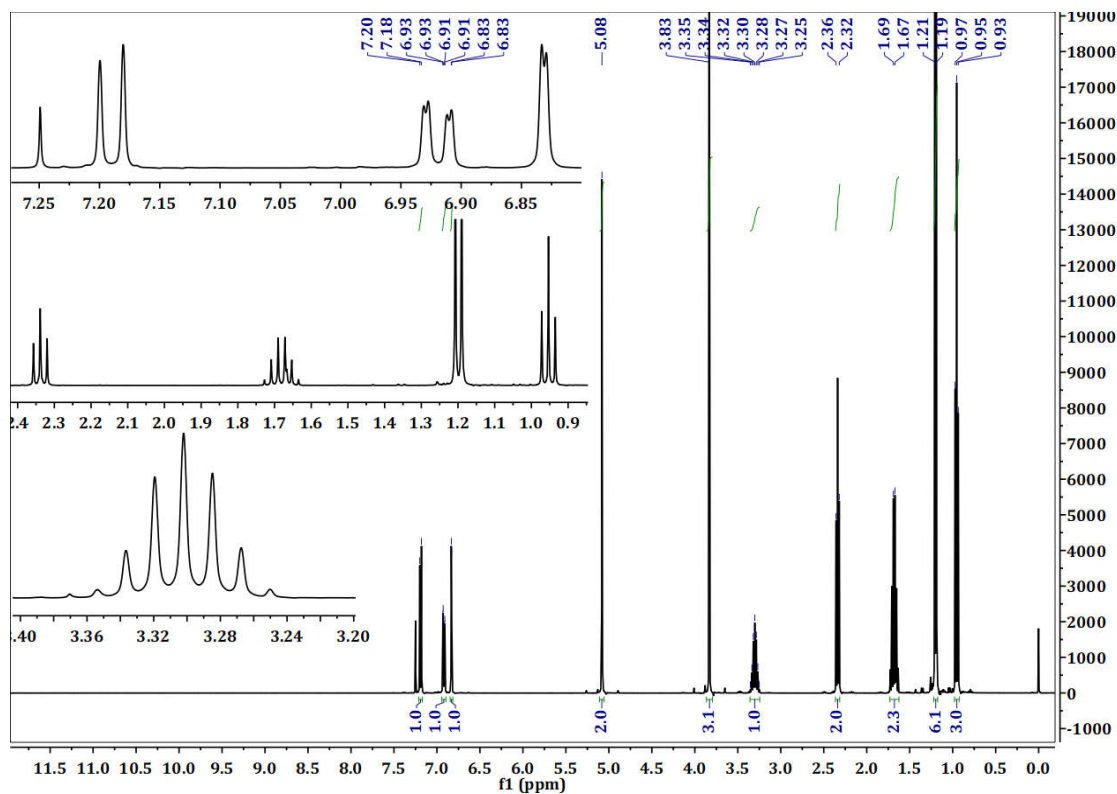


Figure S11. <sup>1</sup>H NMR spectrum of 3-methoxycuminyll butanoate (8).

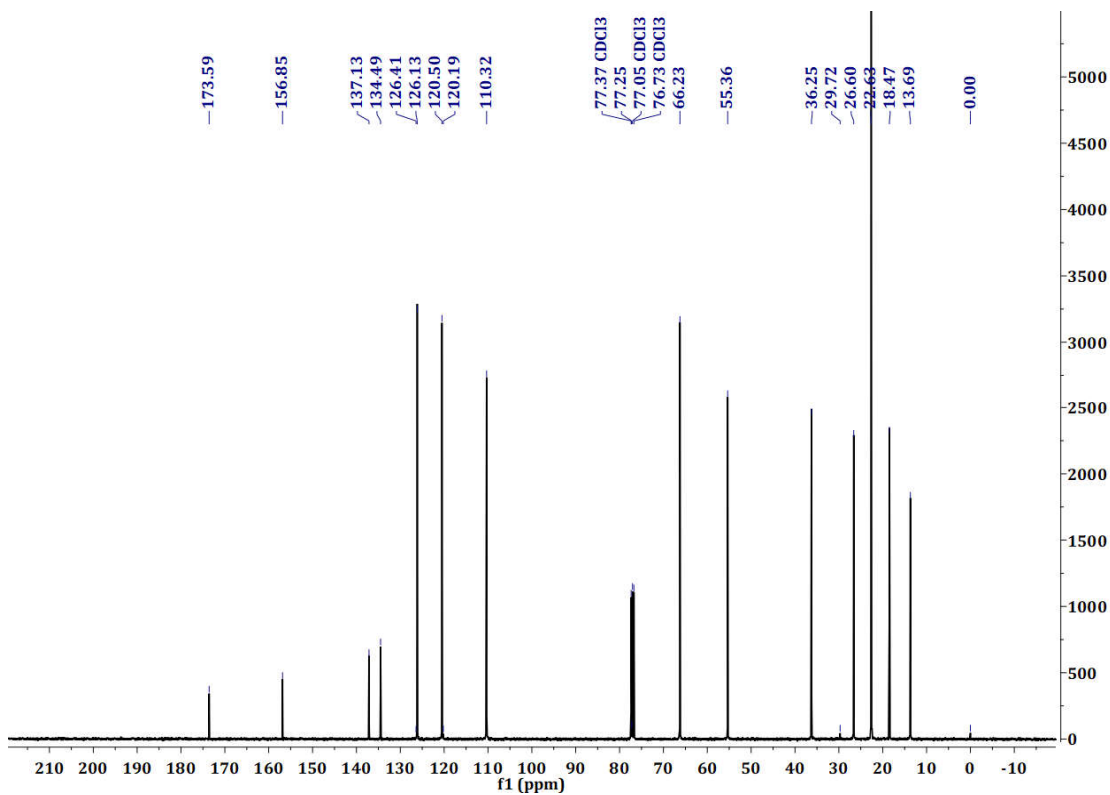
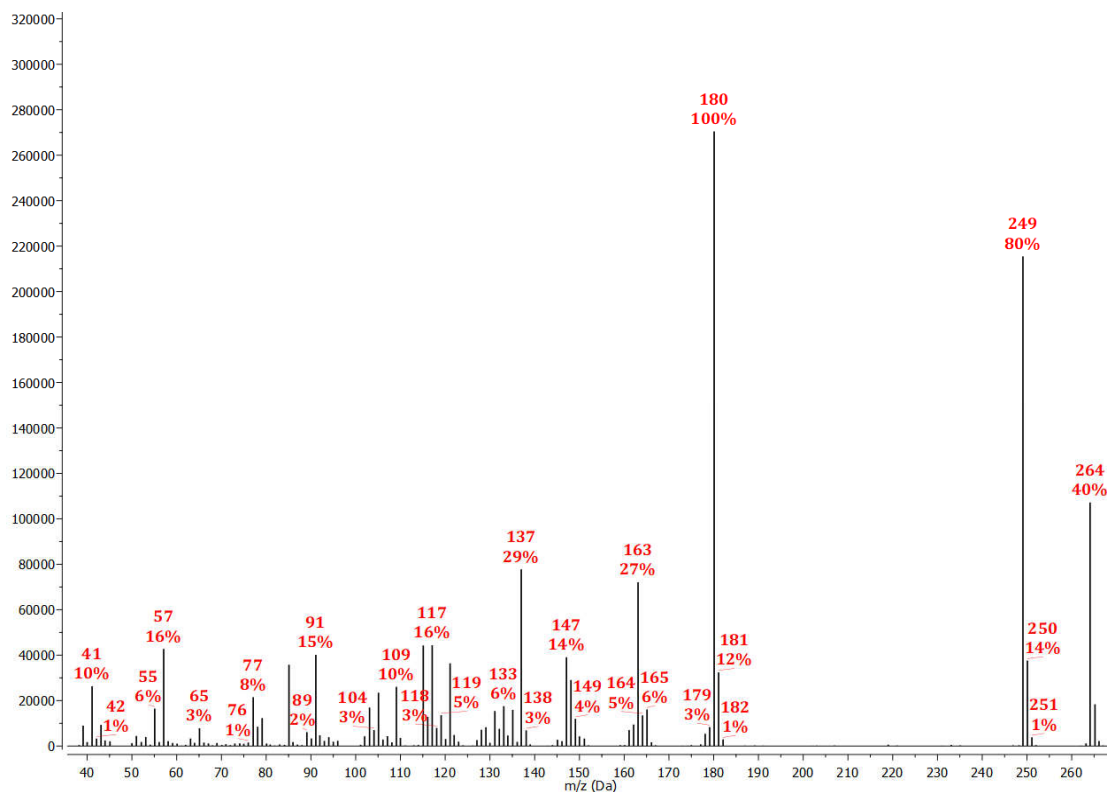
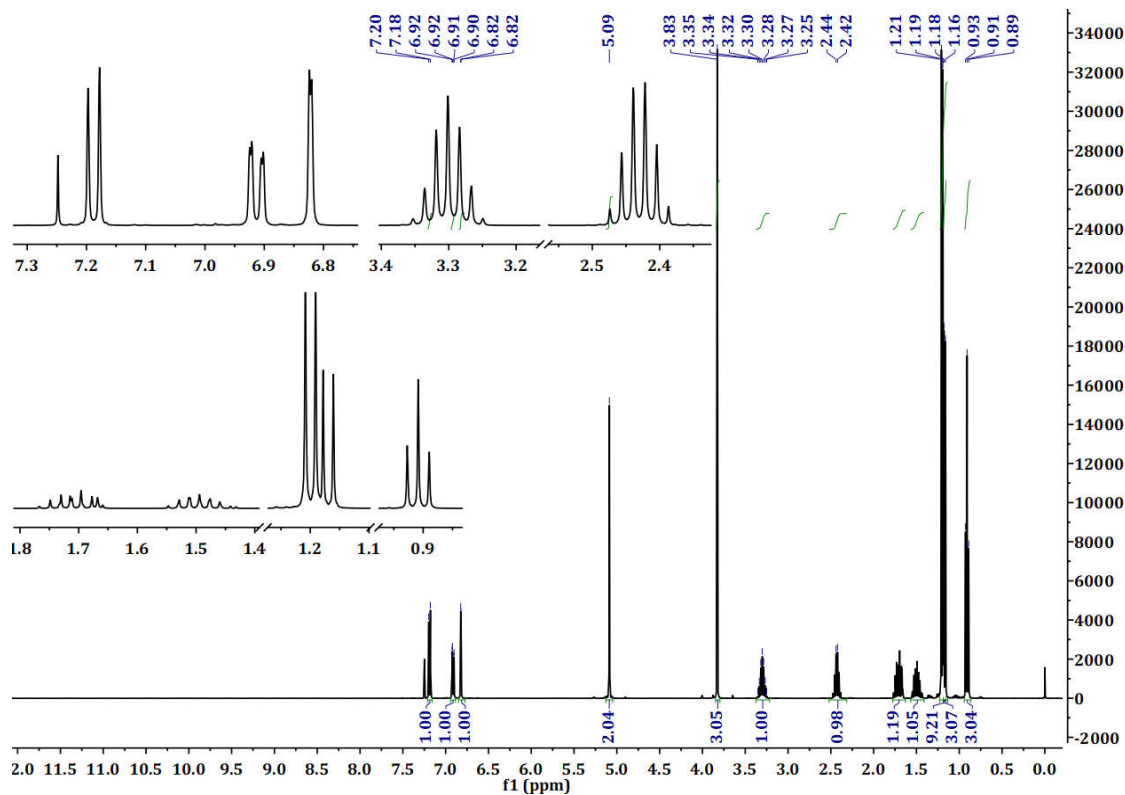


Figure S12. <sup>13</sup>C NMR spectrum of 3-methoxycuminyll butanoate (8).

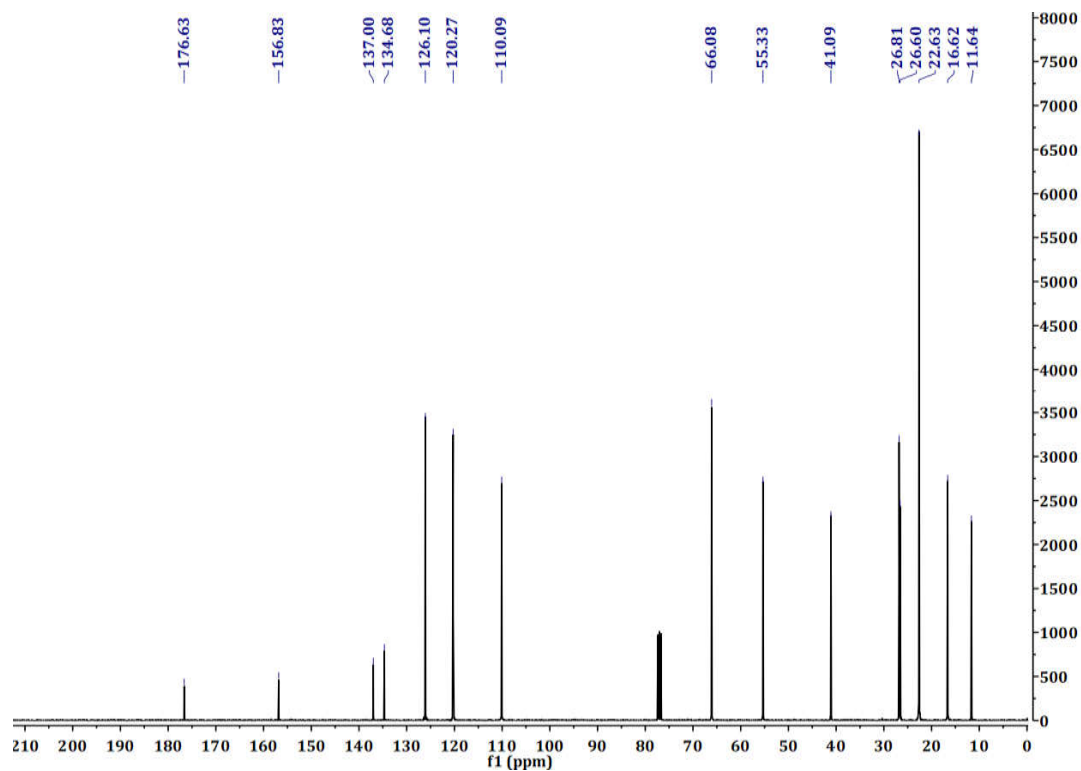




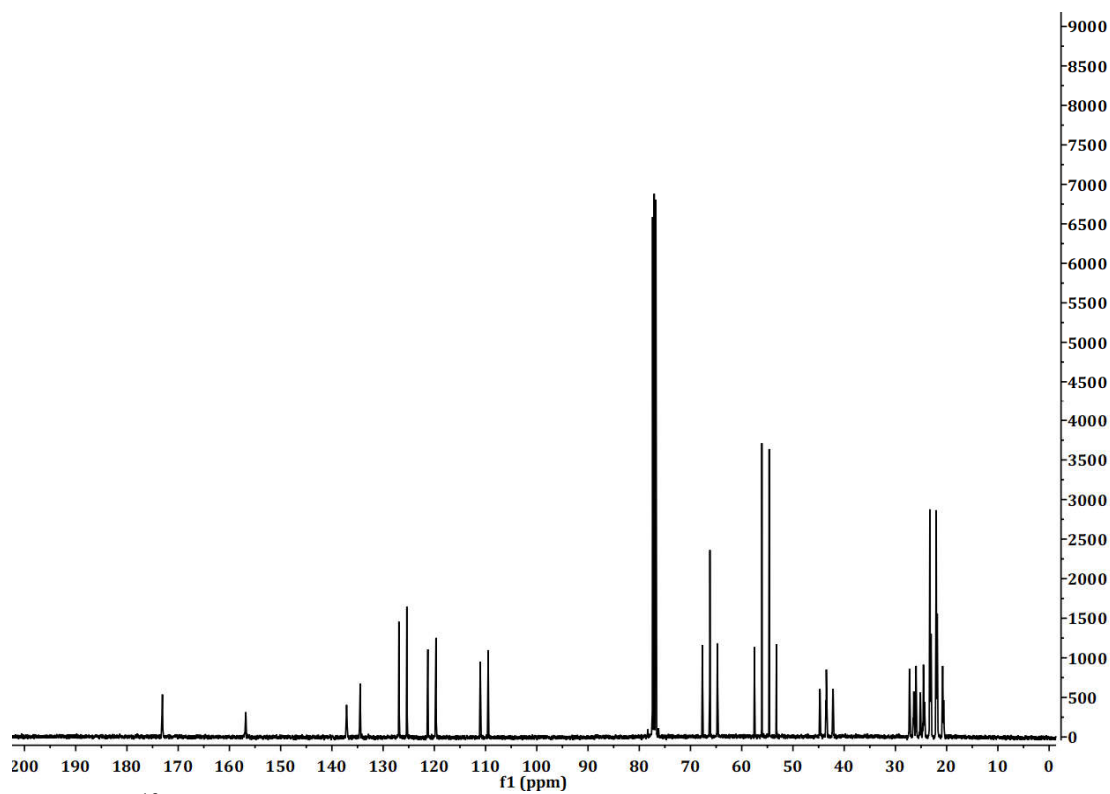
**Figure S13.** Mass spectrum of 3-methoxycuminyll 2-methylbutanoate (**9**).



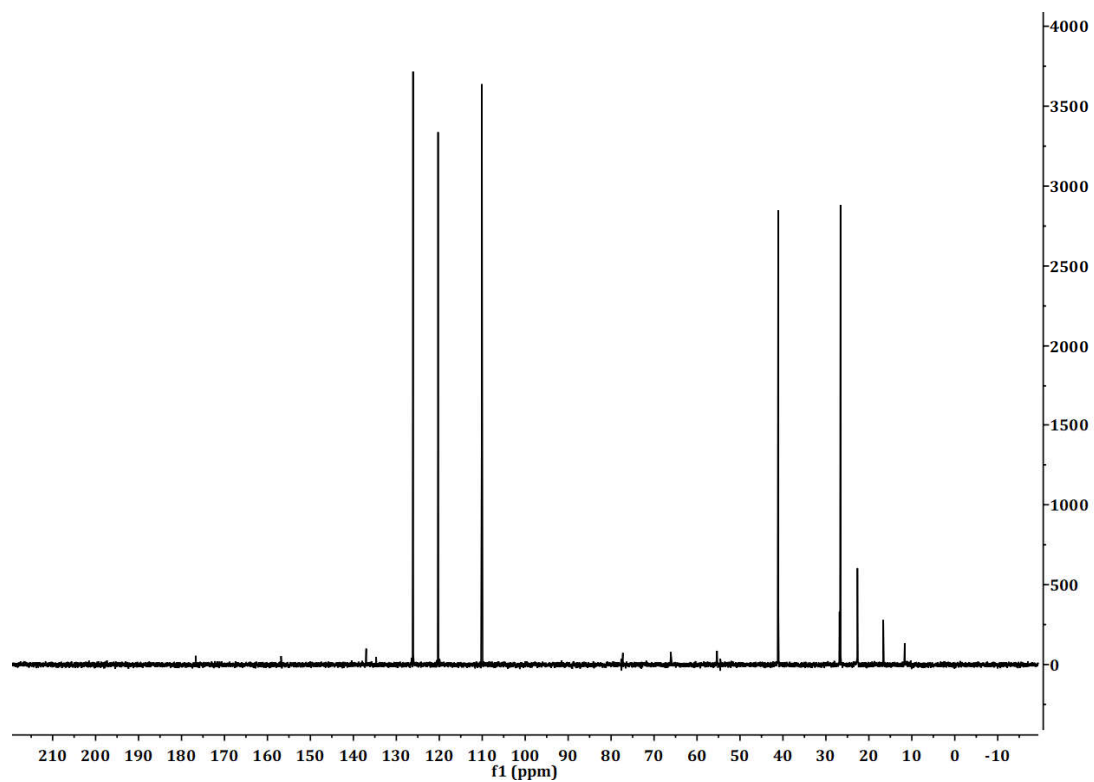
**Figure S14.**  $^1\text{H}$  NMR spectrum of 3-methoxycuminyll 2-methylbutanoate (**9**).



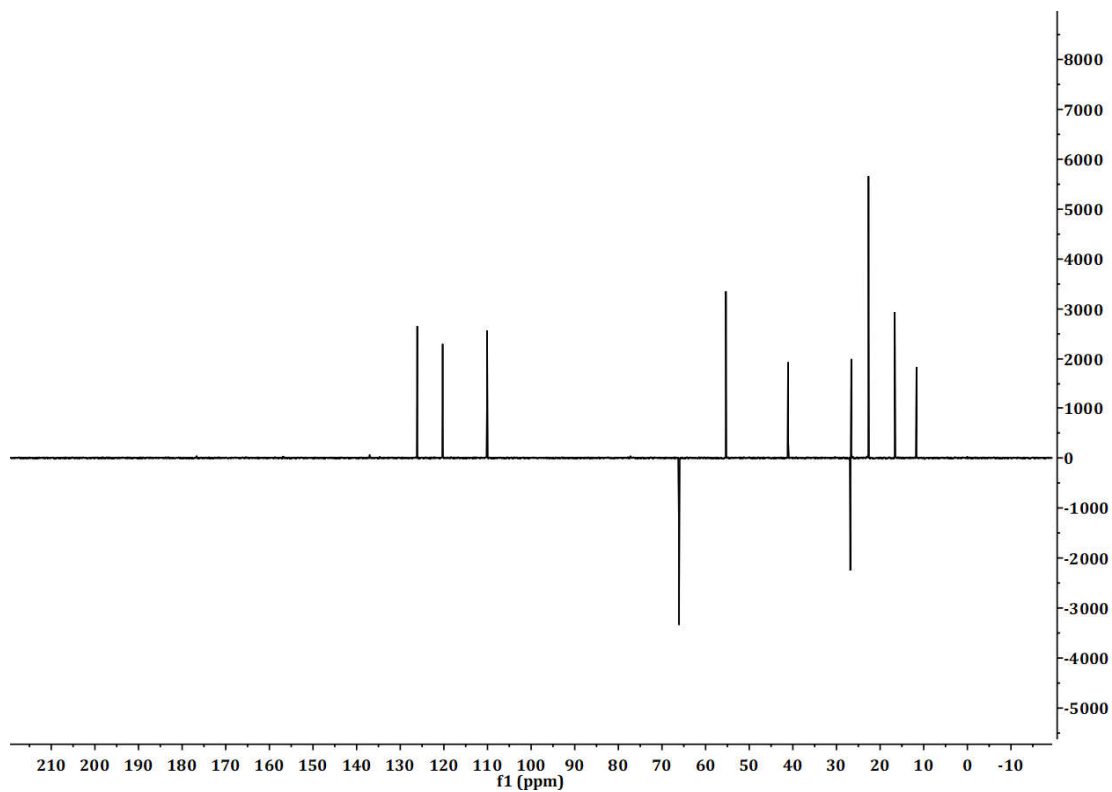
**Figure S15.** <sup>13</sup>C NMR spectrum of 3-methoxycuminylyl 2-methylbutanoate (**9**).



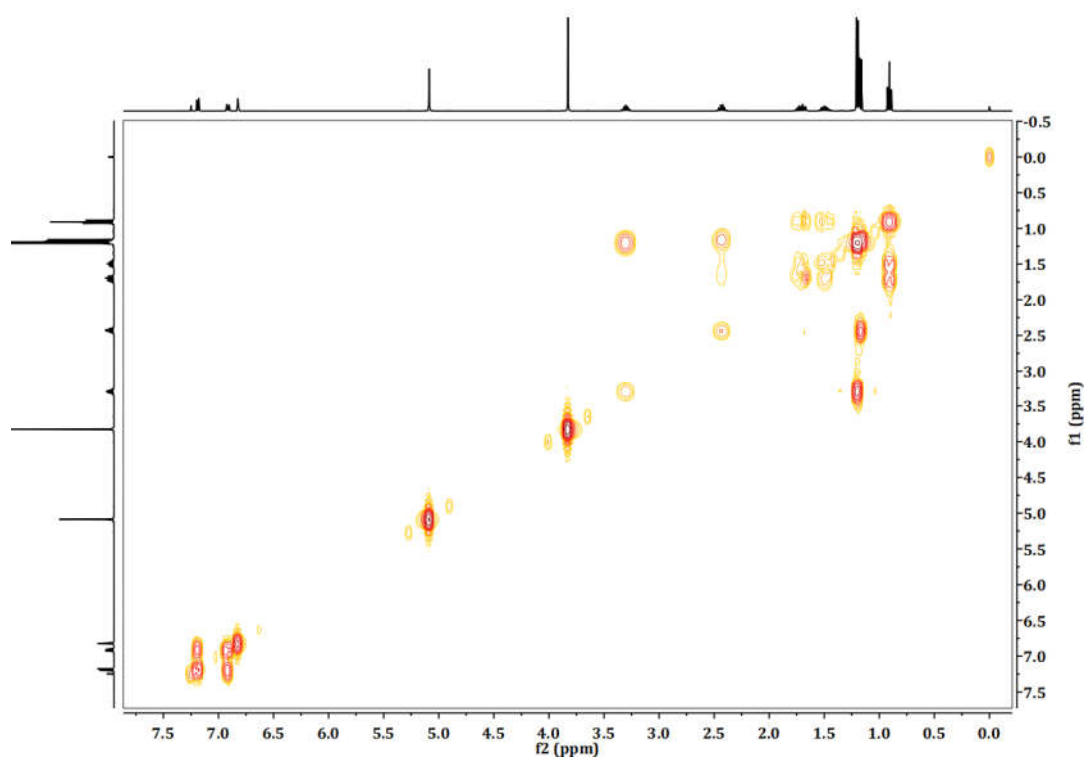
**Figure S16.** <sup>13</sup>C NMR spectrum (without heteronuclear decoupling) of 3-methoxycuminylyl 2-methylbutanoate (**9**).



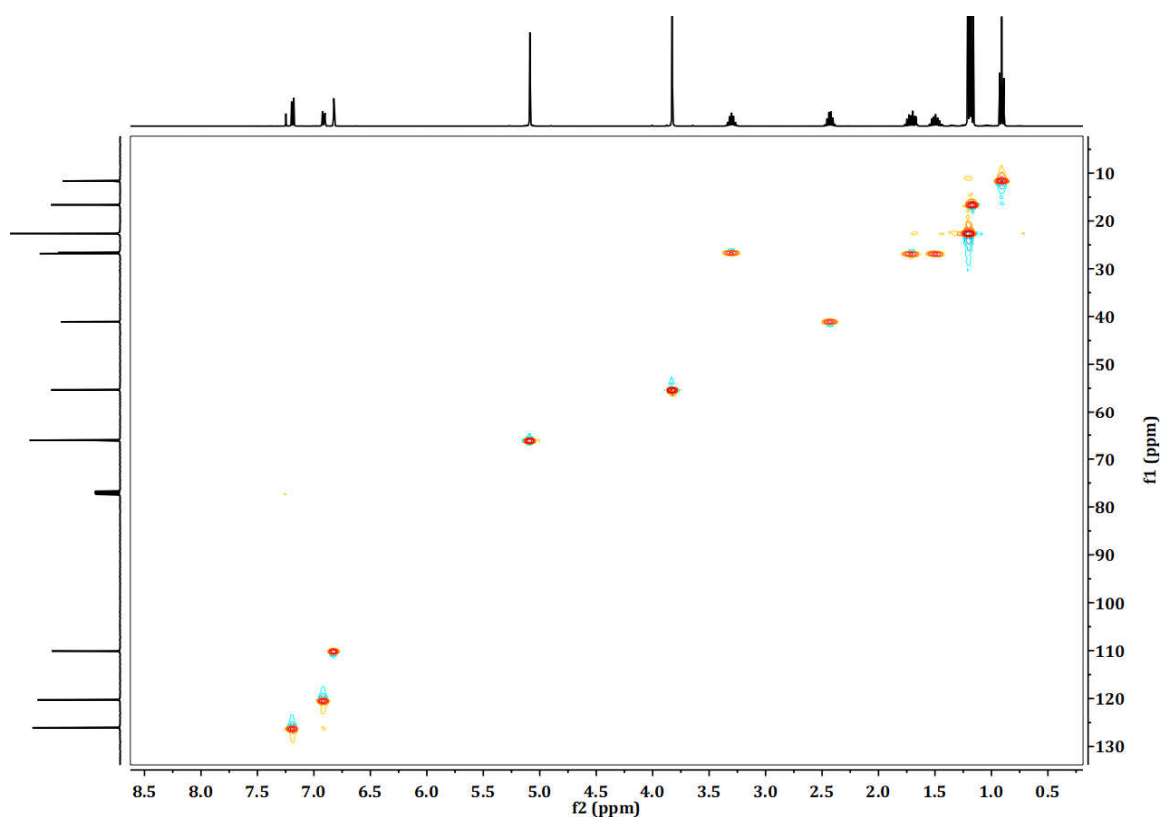
**Figure S17.** Distortionless enhancement by polarization transfer spectrum (DEPT90) of 3-methoxycuminy 2-methylbutanoate (**9**).



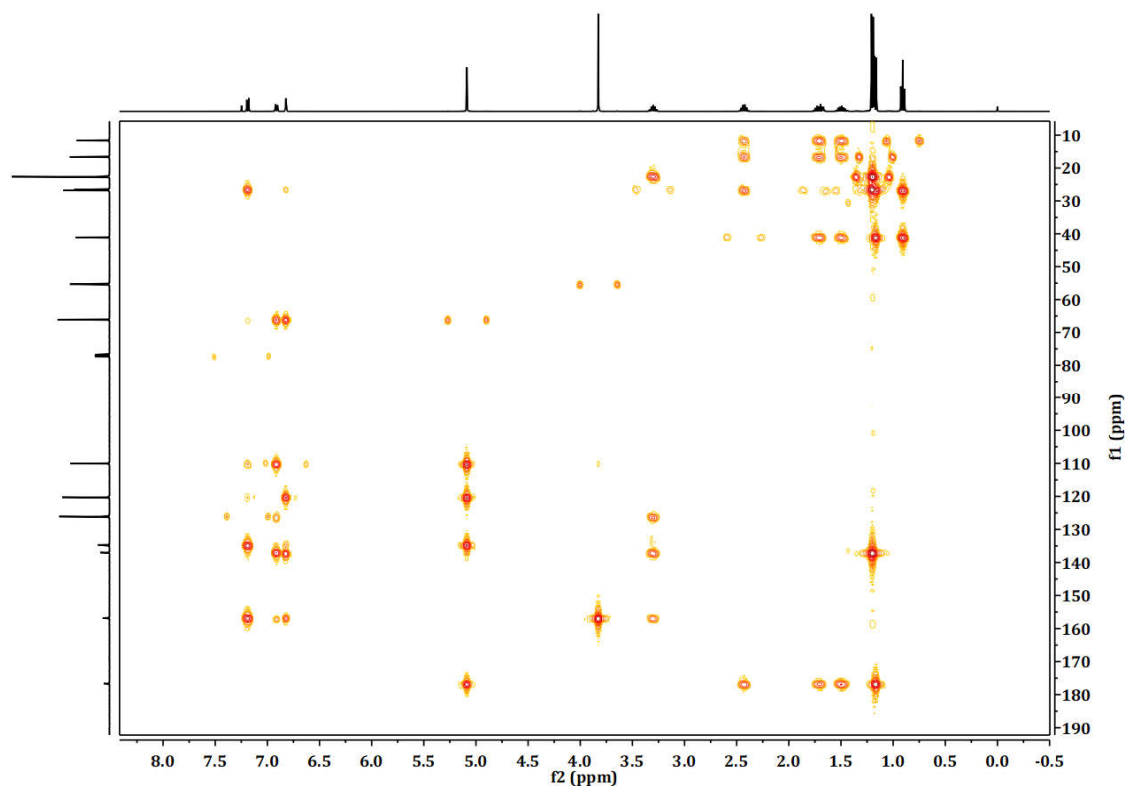
**Figure S18.** Distortionless enhancement by polarization transfer spectrum (DEPT135) of 3-methoxycuminy 2-methylbutanoate (**9**).



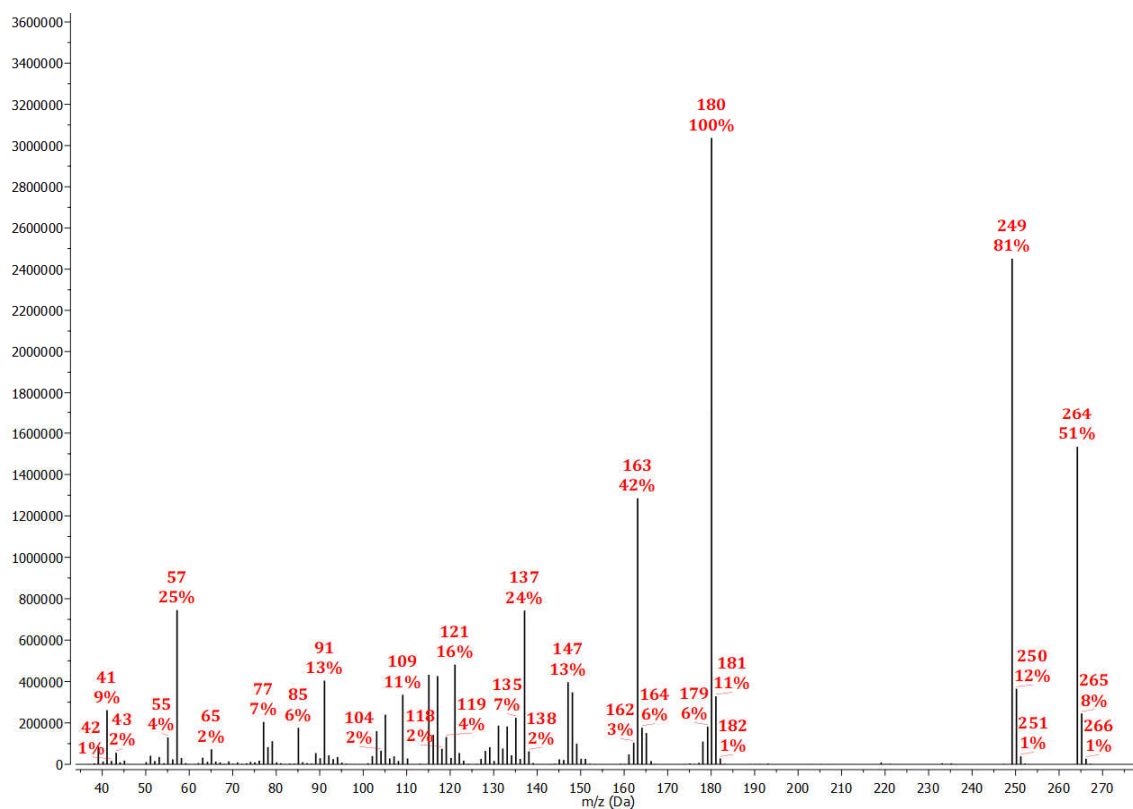
**Figure S19.** Gradient  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of 3-methoxycuminylyl 2-methylbutanoate (**9**).



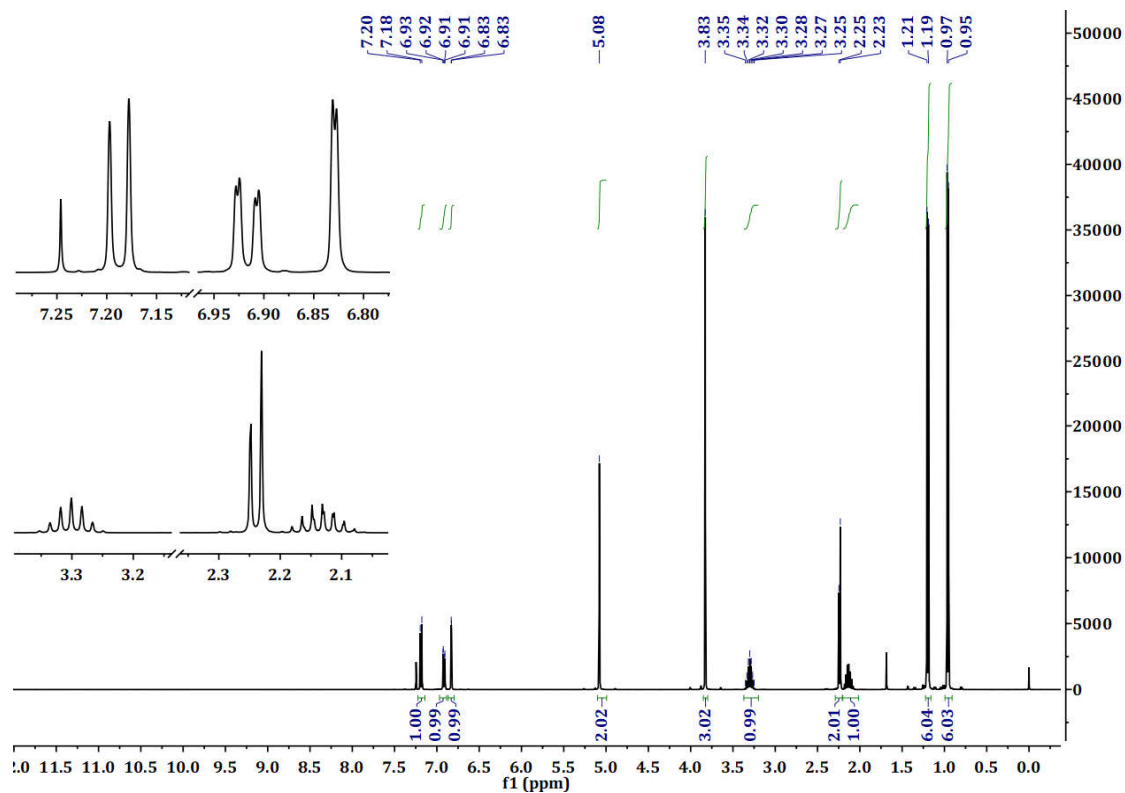
**Figure S20.** Gradient HSQC spectrum of 3-methoxycuminylyl 2-methylbutanoate (**9**).



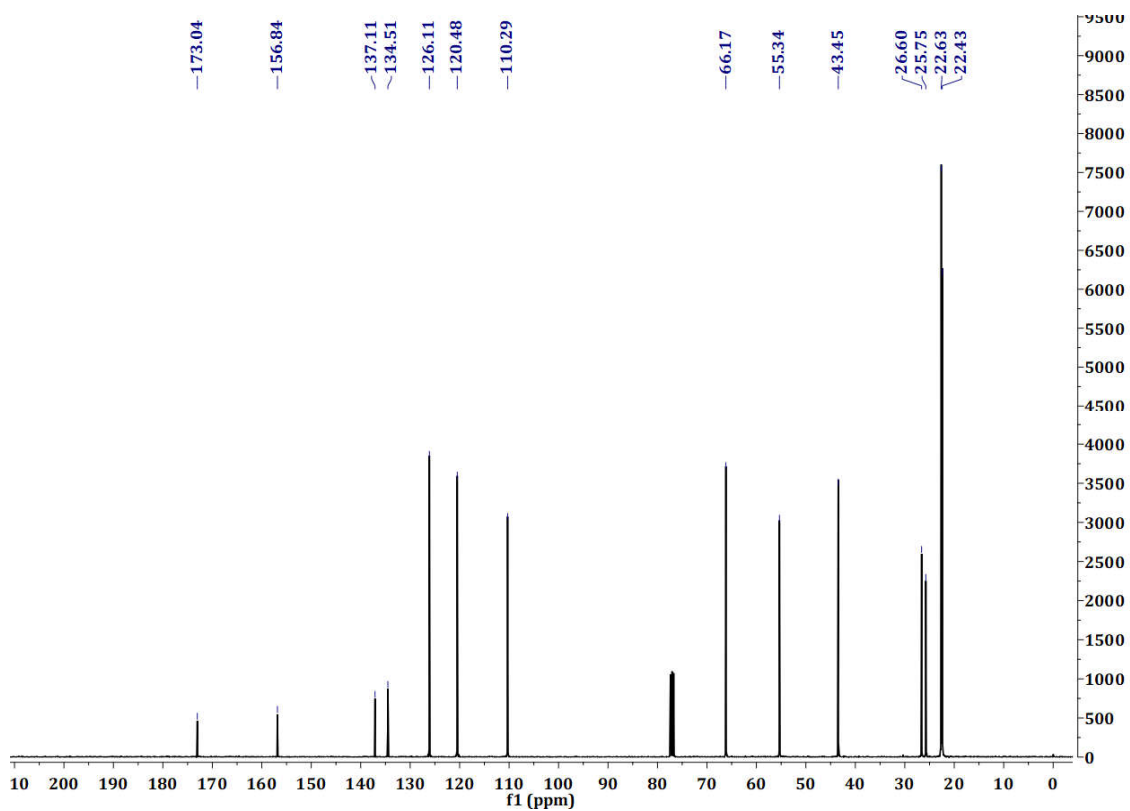
**Figure S21.** Gradient HMBC spectrum of 3-methoxycuminyll 2-methylbutanoate (**9**).



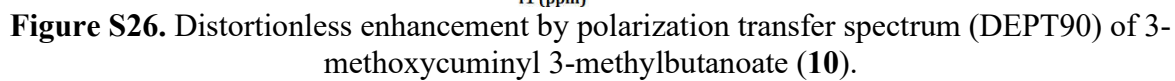
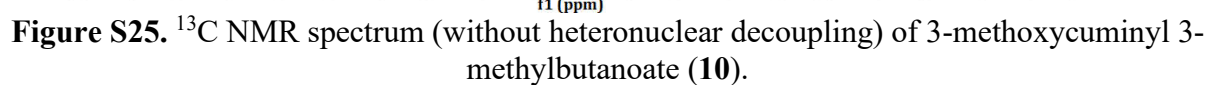
**Figure S22.** Mass spectrum of 3-methoxycuminyll 3-methylbutanoate (**10**).

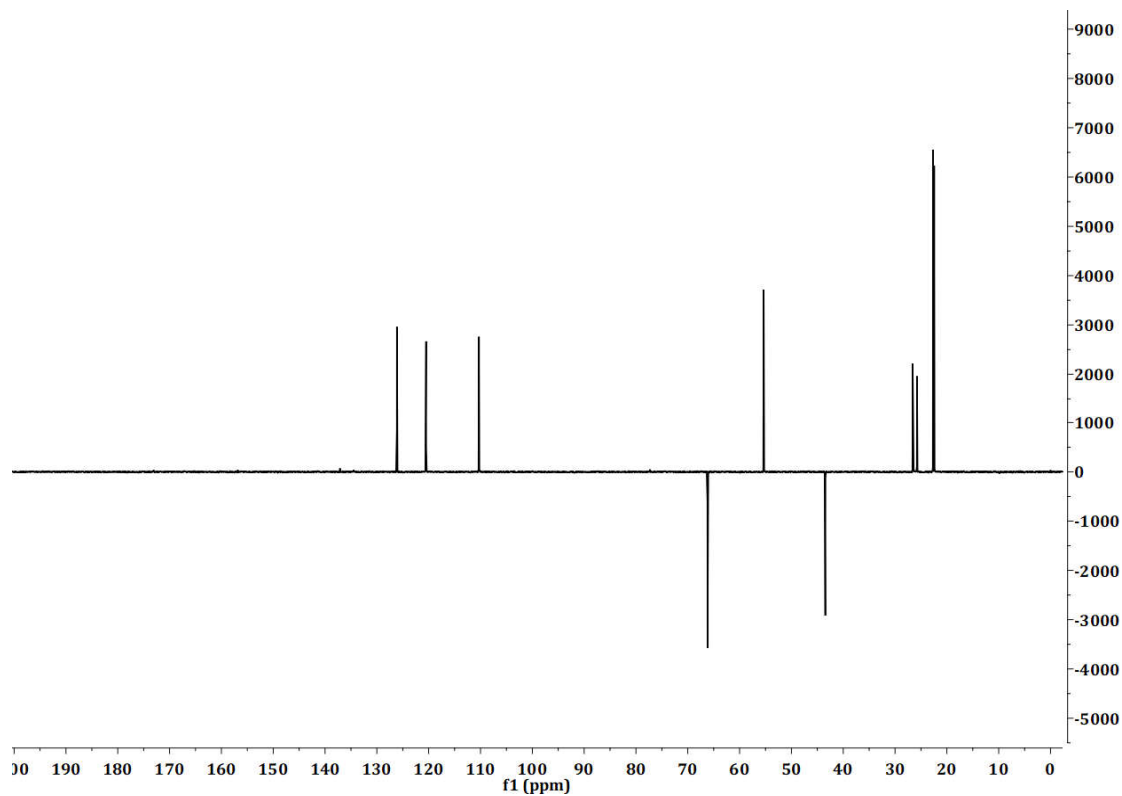


**Figure S23.** <sup>1</sup>H NMR spectrum of 3-methoxycuminy 3-methylbutanoate (**10**).

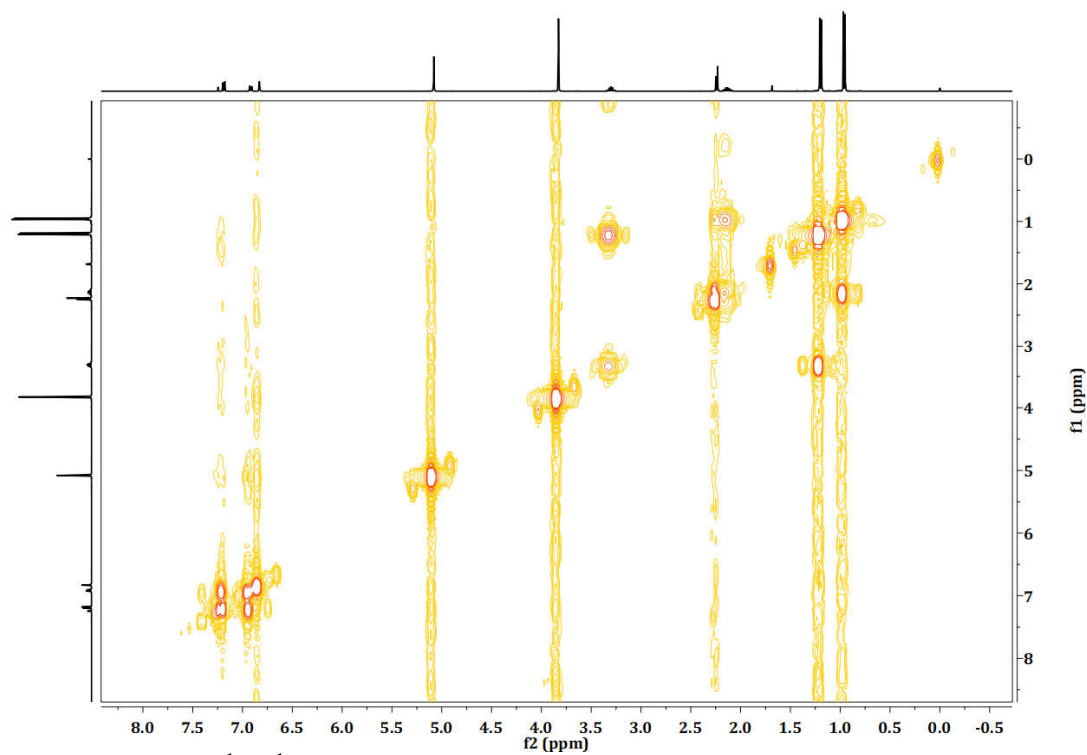


**Figure S24.** <sup>13</sup>C NMR spectrum of 3-methoxycuminy 3-methylbutanoate (**10**).



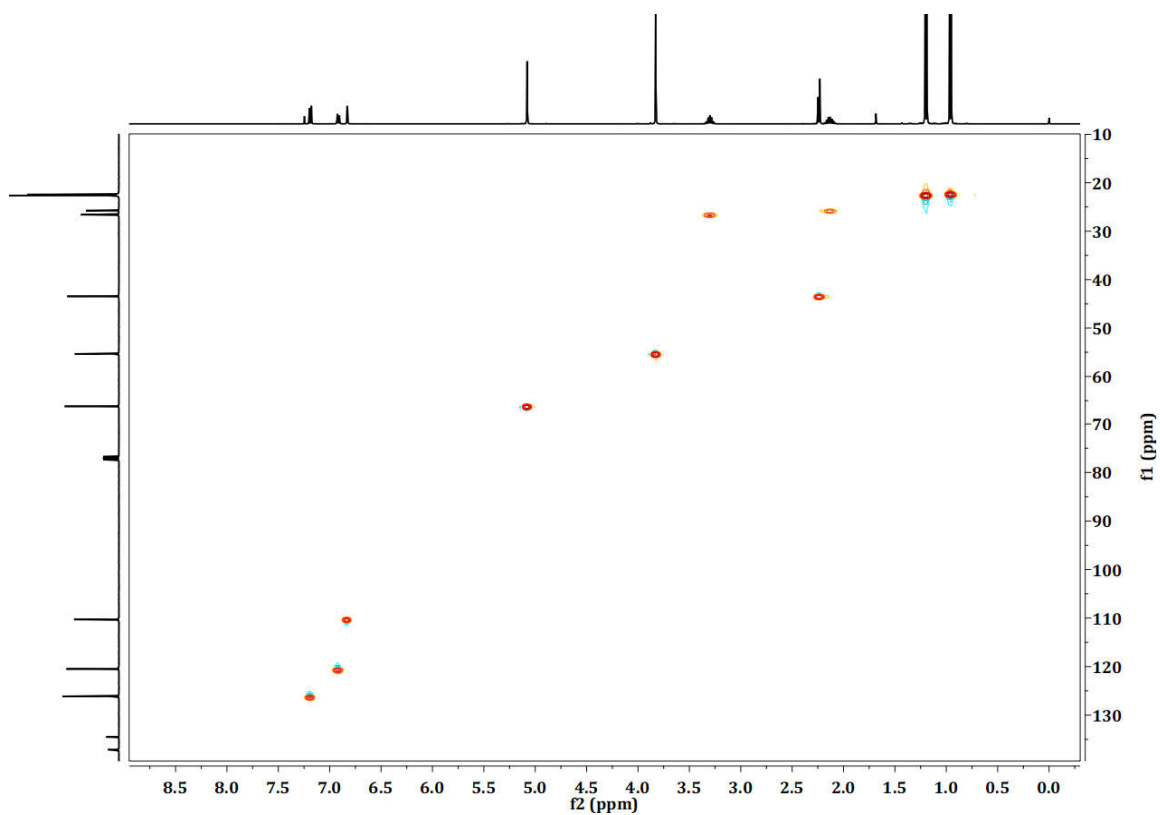


**Figure S27.** Distortionless enhancement by polarization transfer spectrum (DEPT135) of 3-methoxycuminy 3-methylbutanoate (**10**).

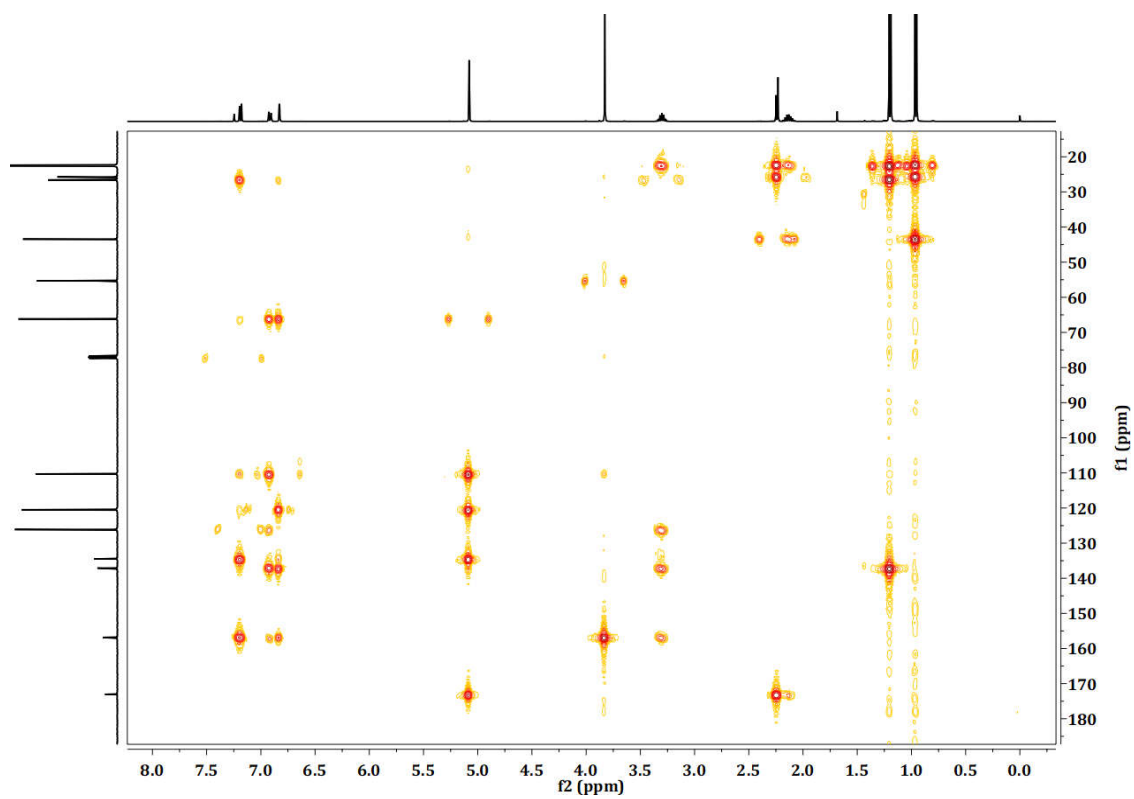


**Figure S28.** Gradient  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of 3-methoxycuminy 3-methylbutanoate (**10**).

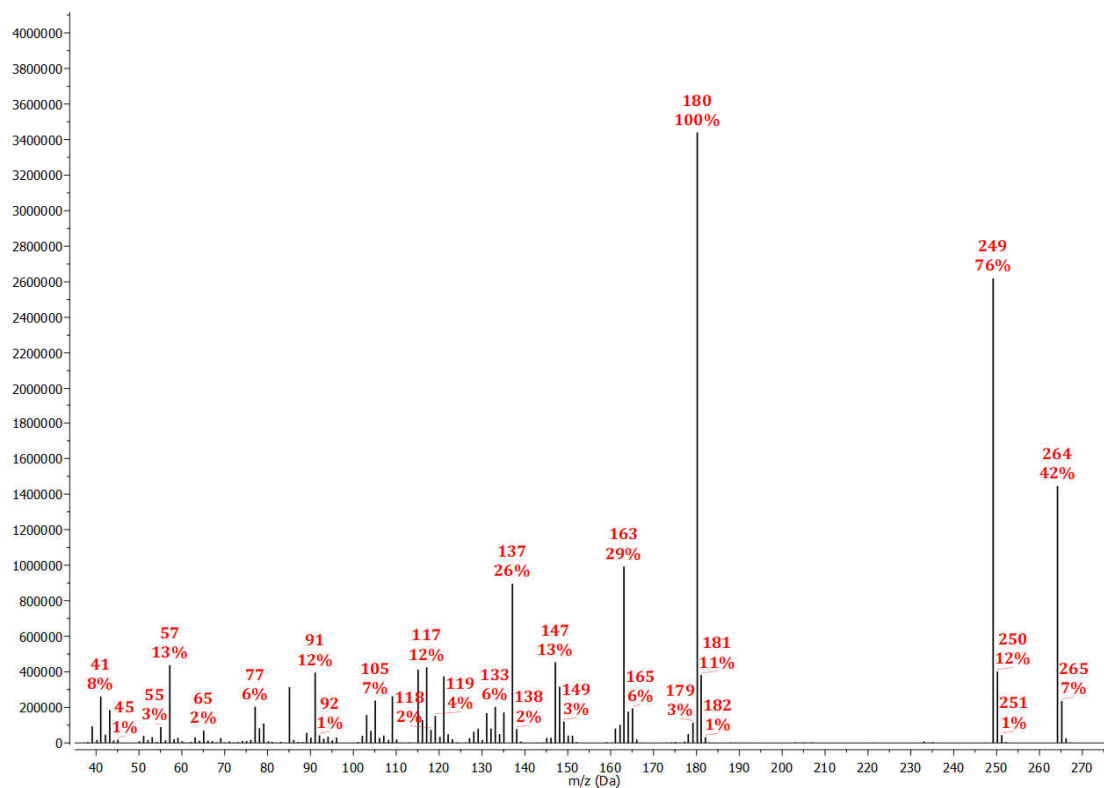




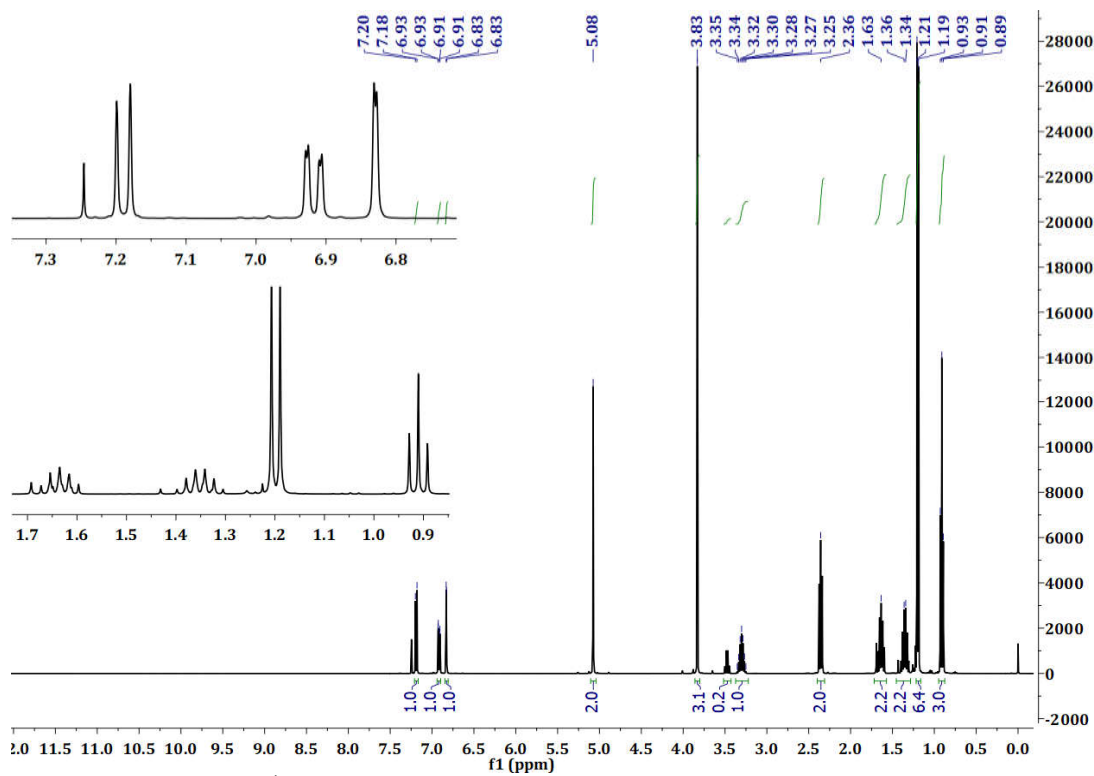
**Figure S29.** Gradient HSQC spectrum of 3-methoxycuminylyl 3-methylbutanoate (**10**).



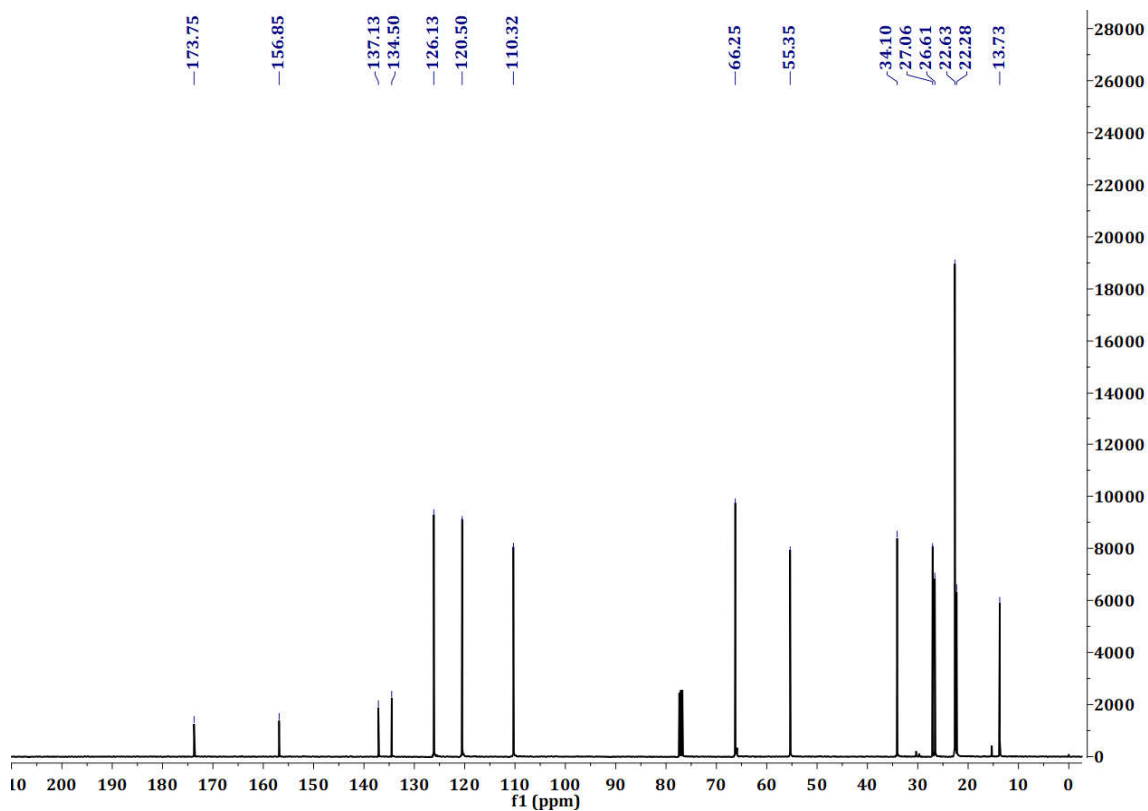
**Figure S30.** Gradient HMBC spectrum of 3-methoxycuminylyl 3-methylbutanoate (**10**).



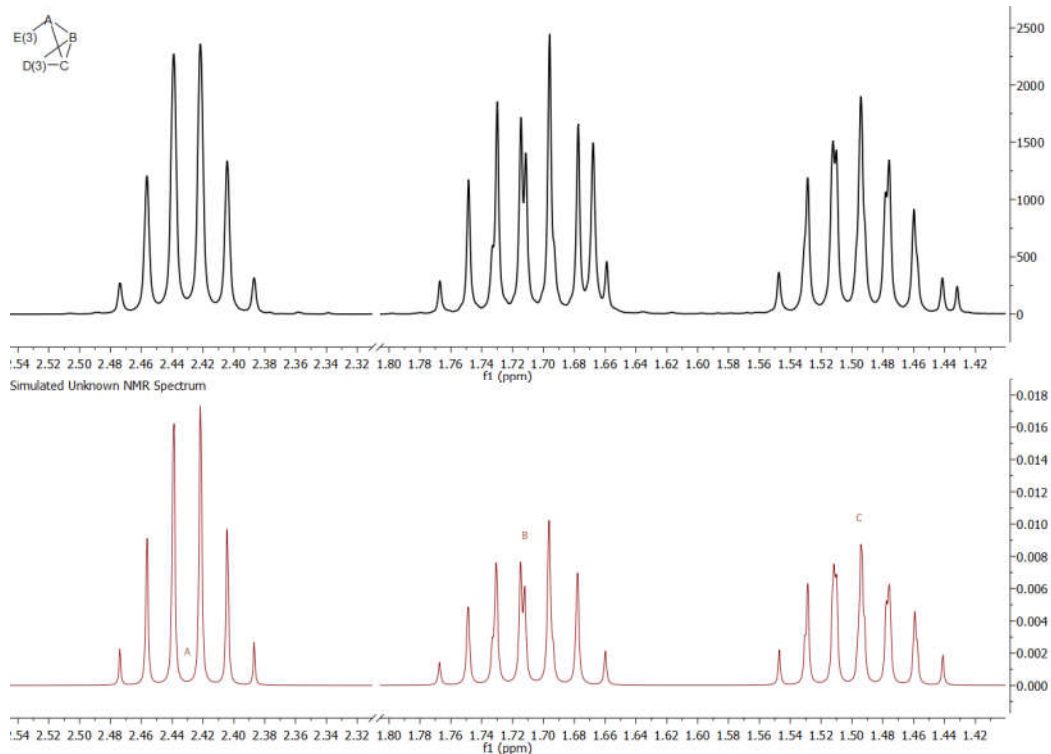
**Figure S31.** Mass spectrum of 3-methoxycuminyll pentanoate (**11**).



**Figure S32.**  $^1\text{H}$  NMR spectrum of 3-methoxycuminyll pentanoate (**11**).



**Figure S33.**  $^{13}\text{C}$  NMR spectrum of 3-methoxycuminyll pentanoate (**11**).



**Figure S34.** Spin simulation of the  $^1\text{H}$  NMR signals for the protons at position 13 and 14 (lower) and comparison with the experimental ones (upper) for 3-methoxycuminyll 2-methylbutanoate (**9**).