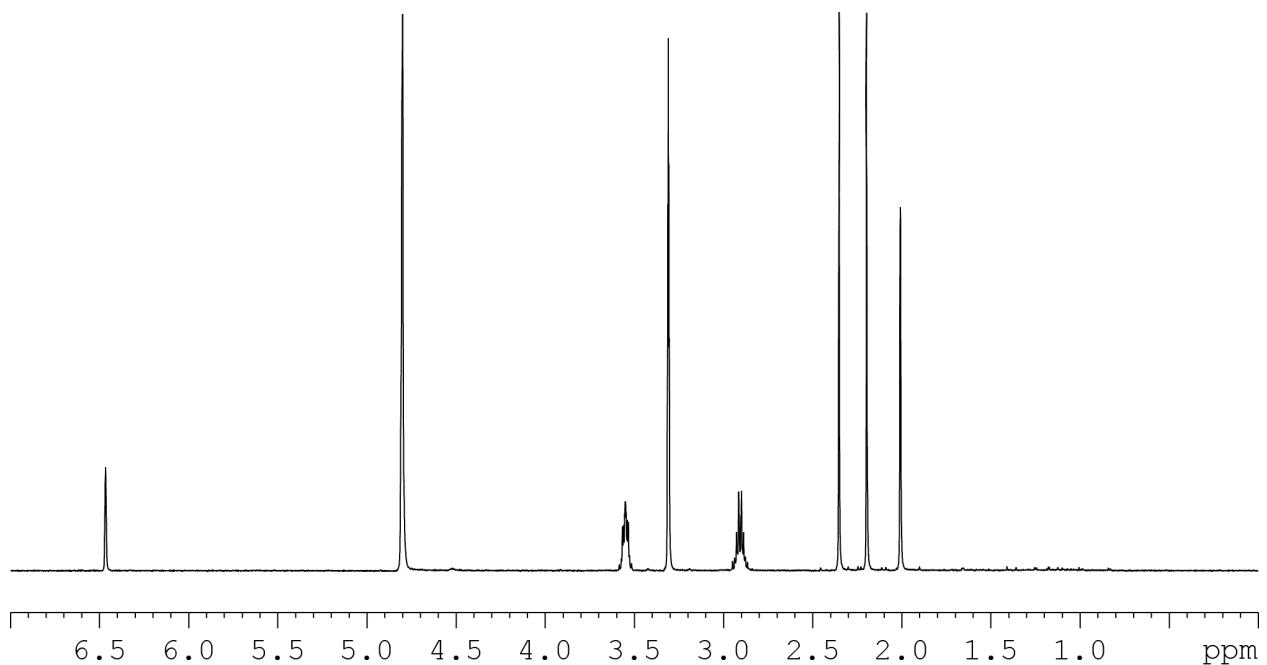


# Supplementary Materials

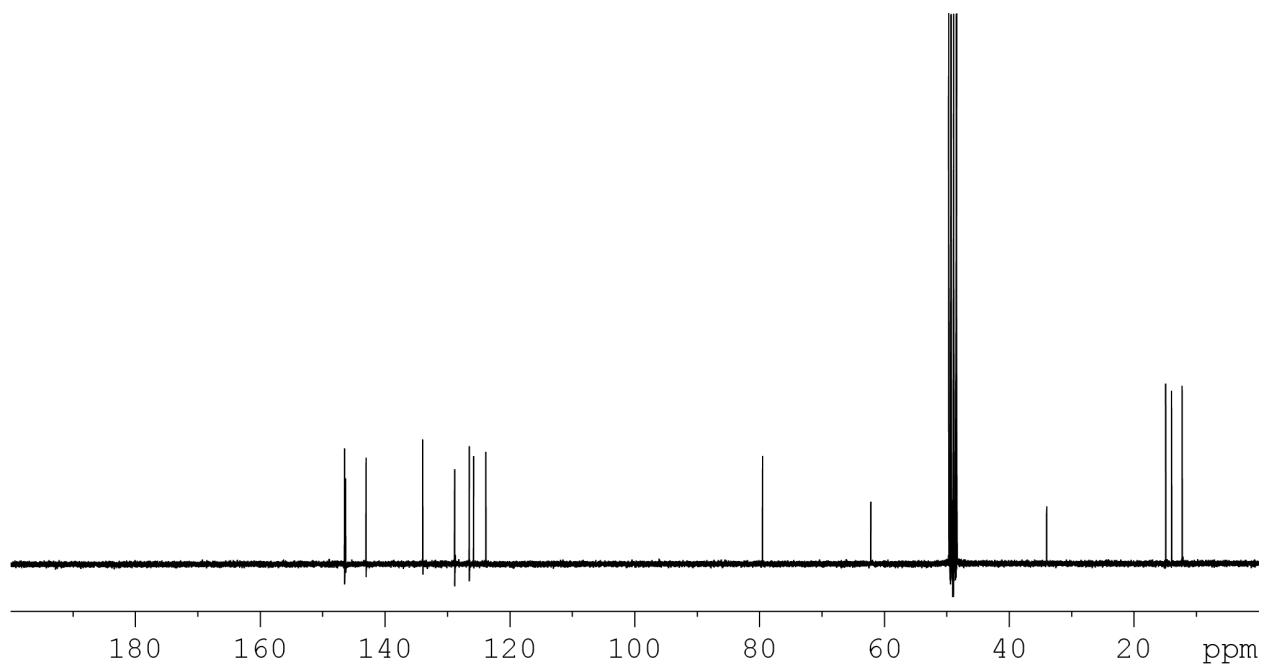
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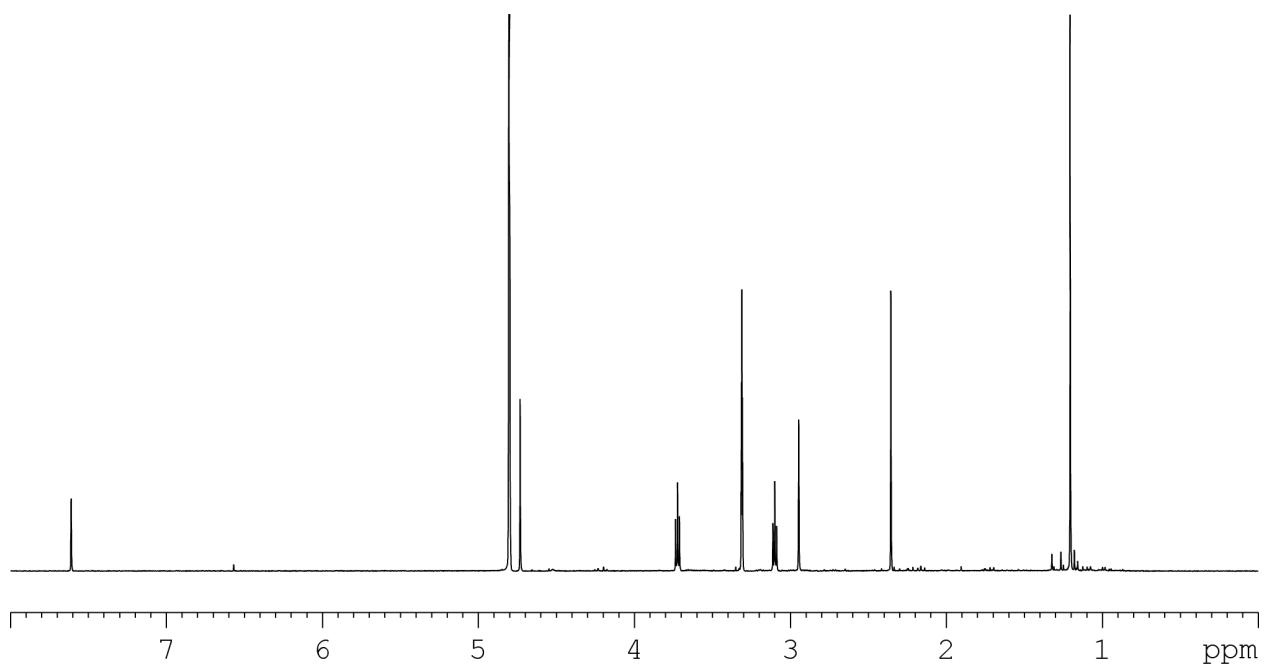
**Figure S1.**  $^1\text{H}$ -NMR (methanol- $d_4$ , 600 MHz) spectrum of **1**.



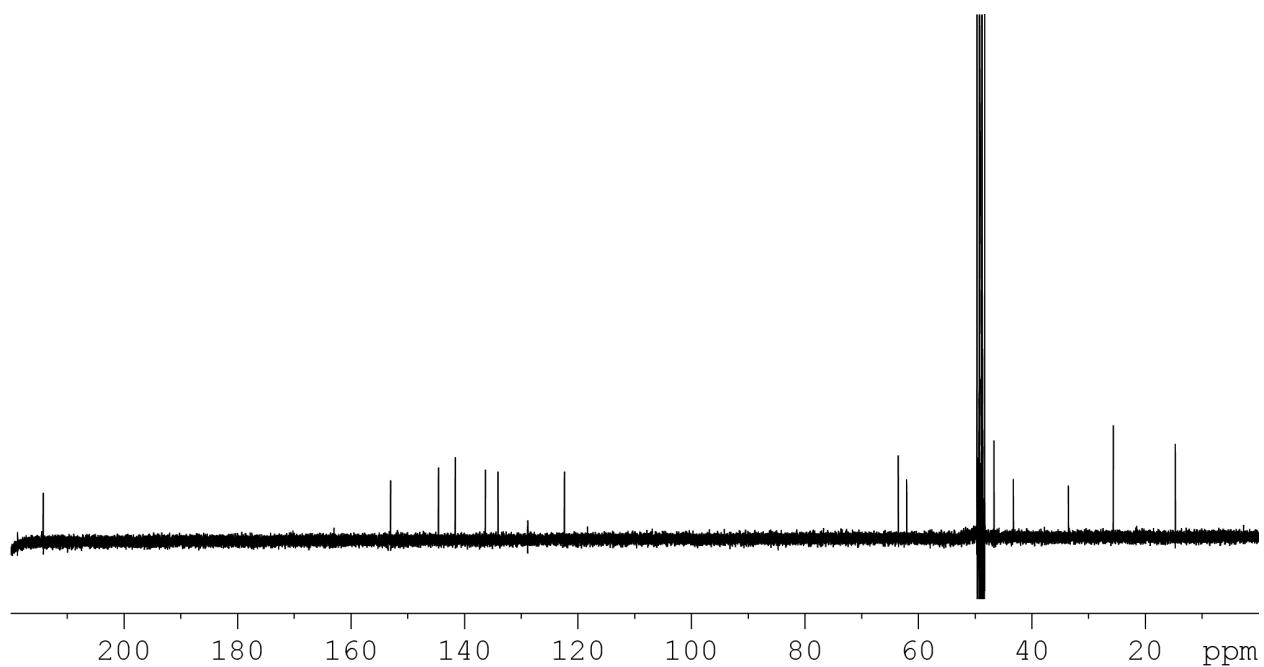
**Figure S2.**  $^{13}\text{C}$ -NMR (methanol- $d_4$ , 100 MHz) spectrum of **1**.



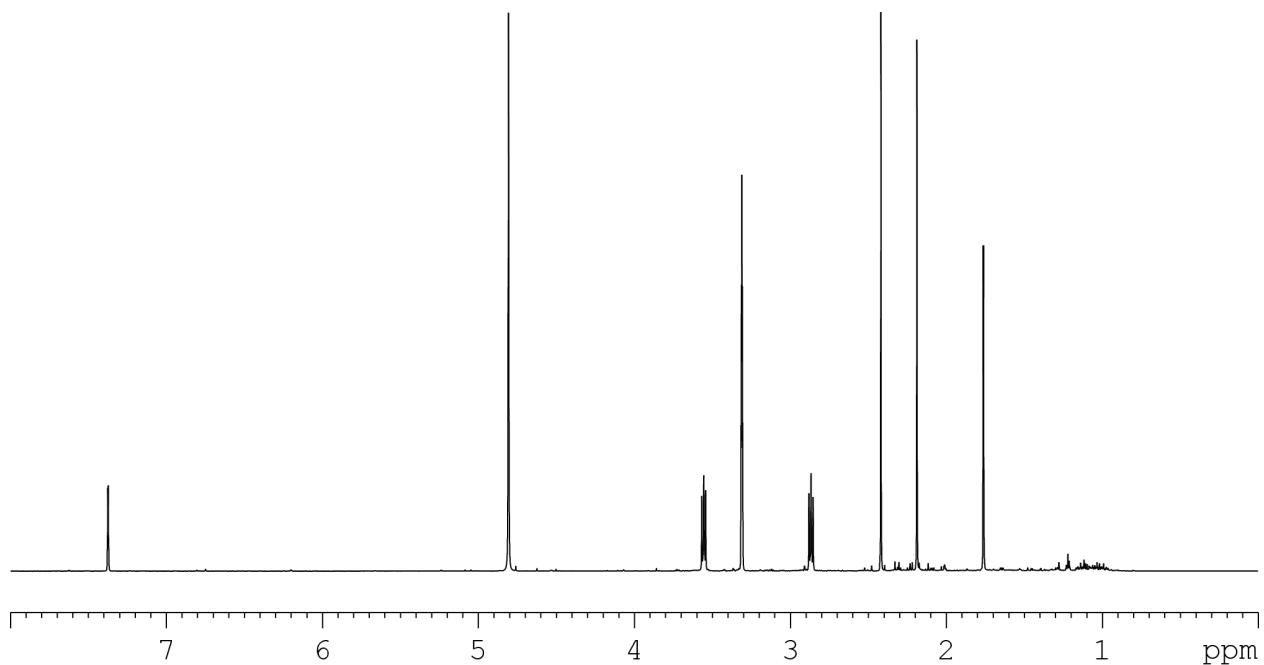
**Figure S3.**  $^1\text{H}$ -NMR (methanol- $d_4$ , 600 MHz) spectrum of **2**.



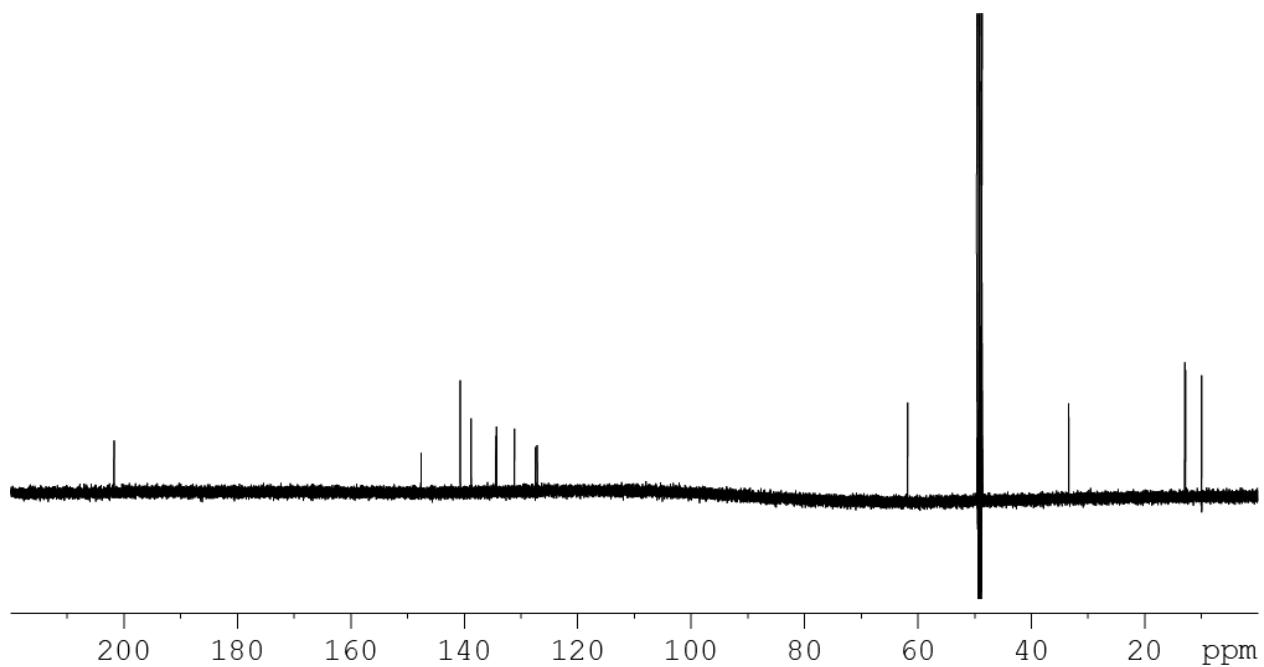
**Figure S4.**  $^{13}\text{C}$ -NMR (methanol- $d_4$ , 100 MHz) spectrum of **2**.



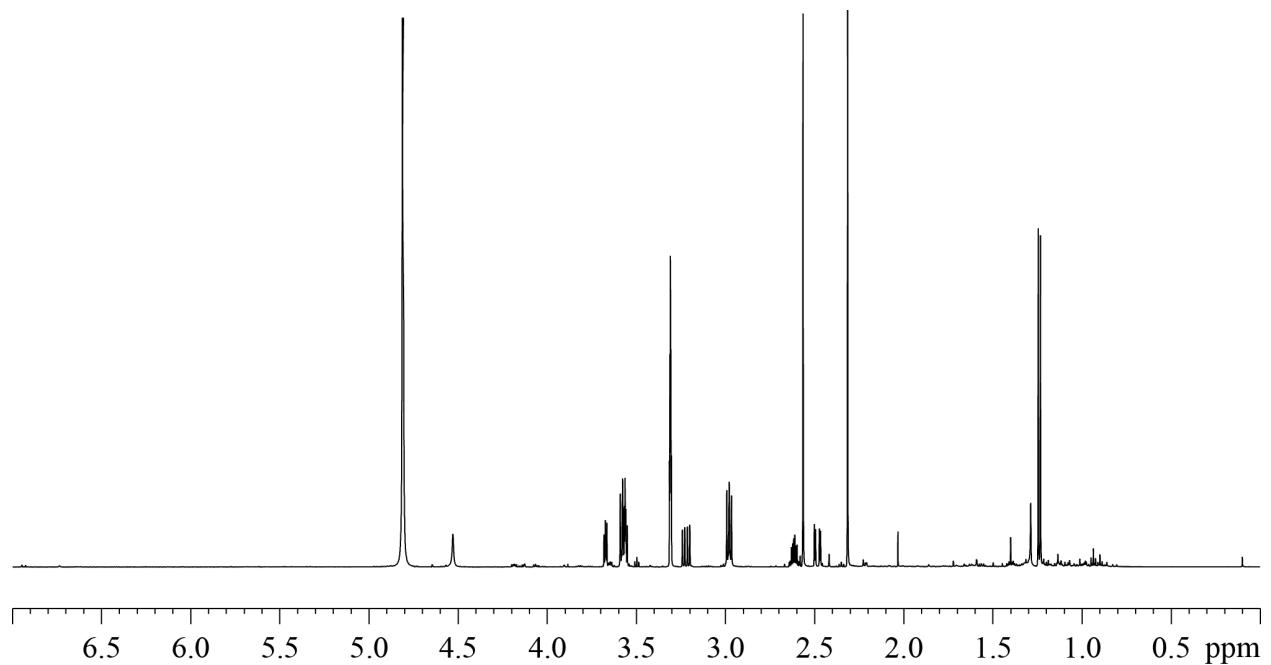
**Figure S5.**  $^1\text{H}$ -NMR (methanol- $d_4$ , 600 MHz) spectrum of **3**.



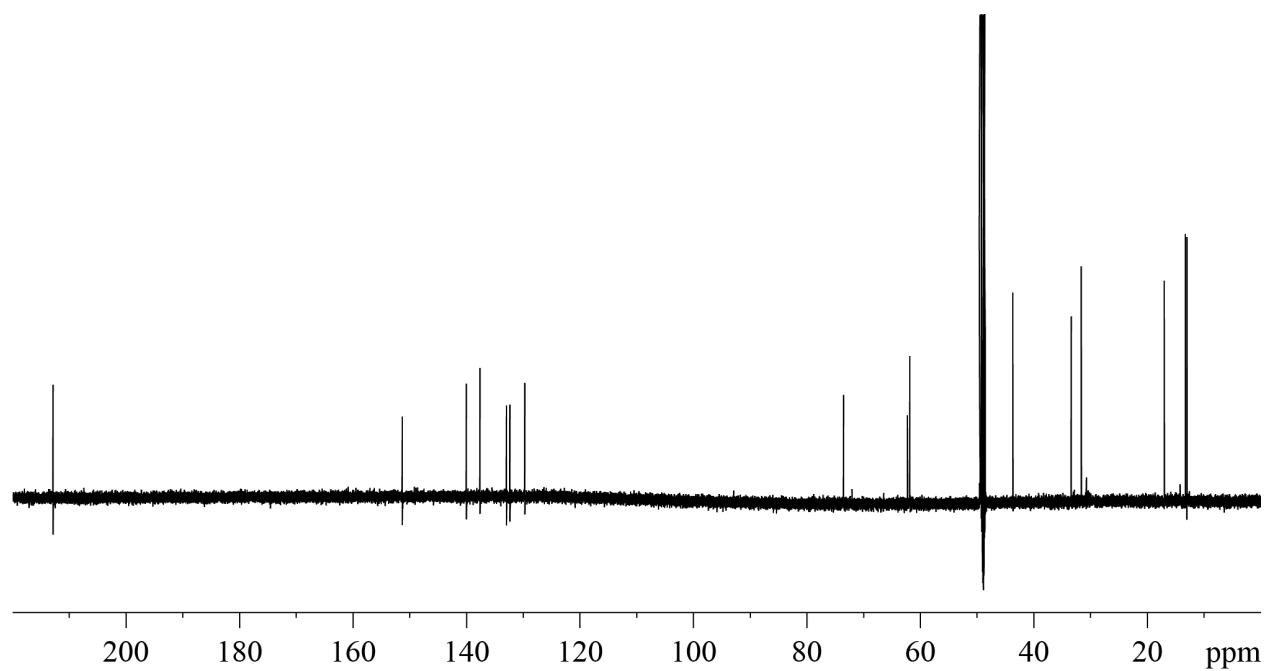
**Figure S6.**  $^{13}\text{C}$ -NMR (methanol- $d_4$ , 100 MHz) spectrum of **3**.



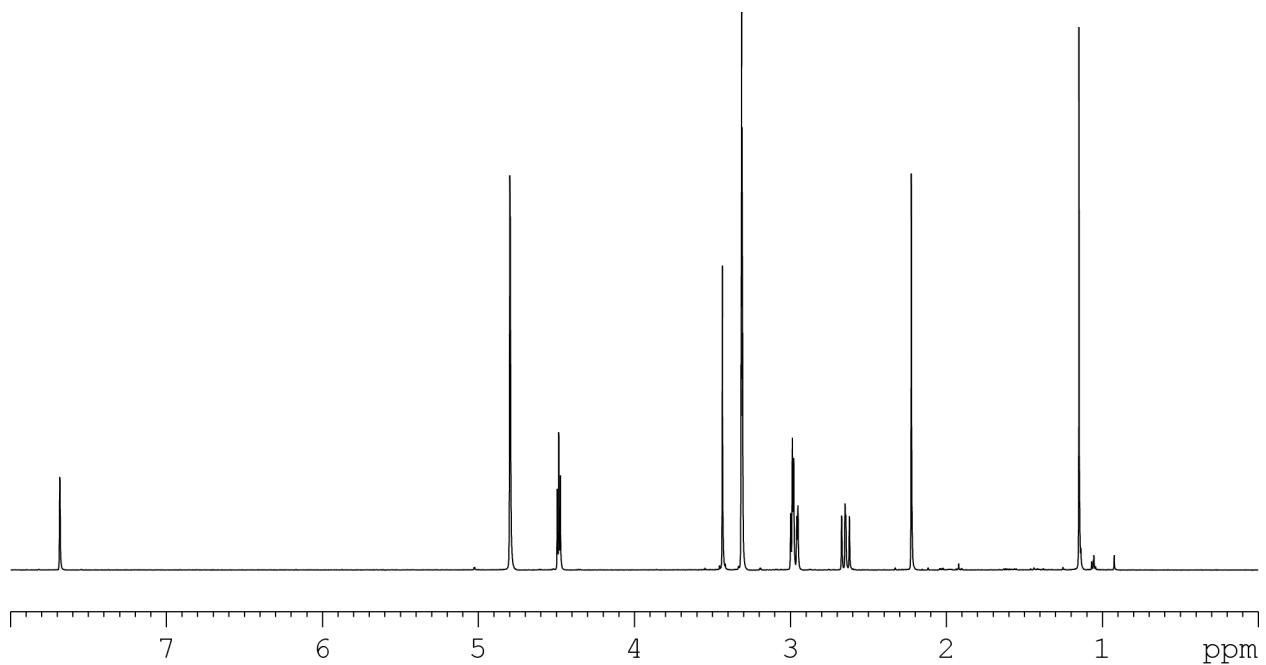
**Figure S7.**  $^1\text{H}$ -NMR (methanol- $d_4$ , 600 MHz) spectrum of pterosin M.



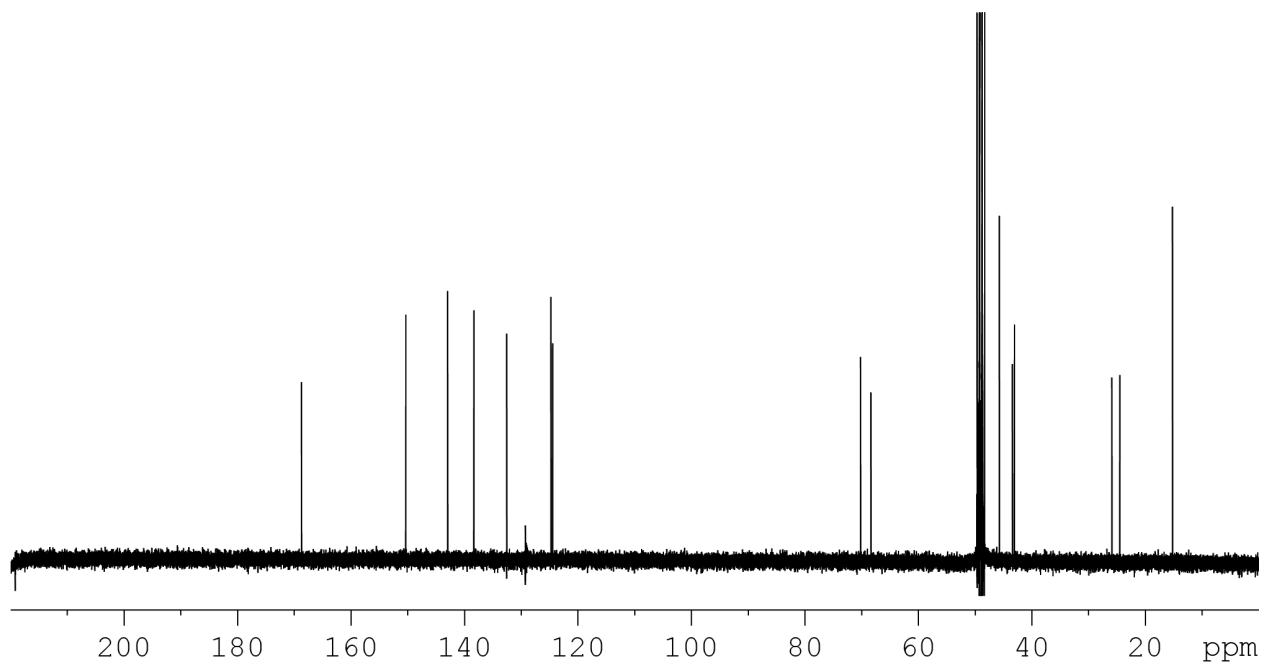
**Figure S8.**  $^{13}\text{C}$ -NMR (methanol- $d_4$ , 100 MHz) spectrum of pterosin M.



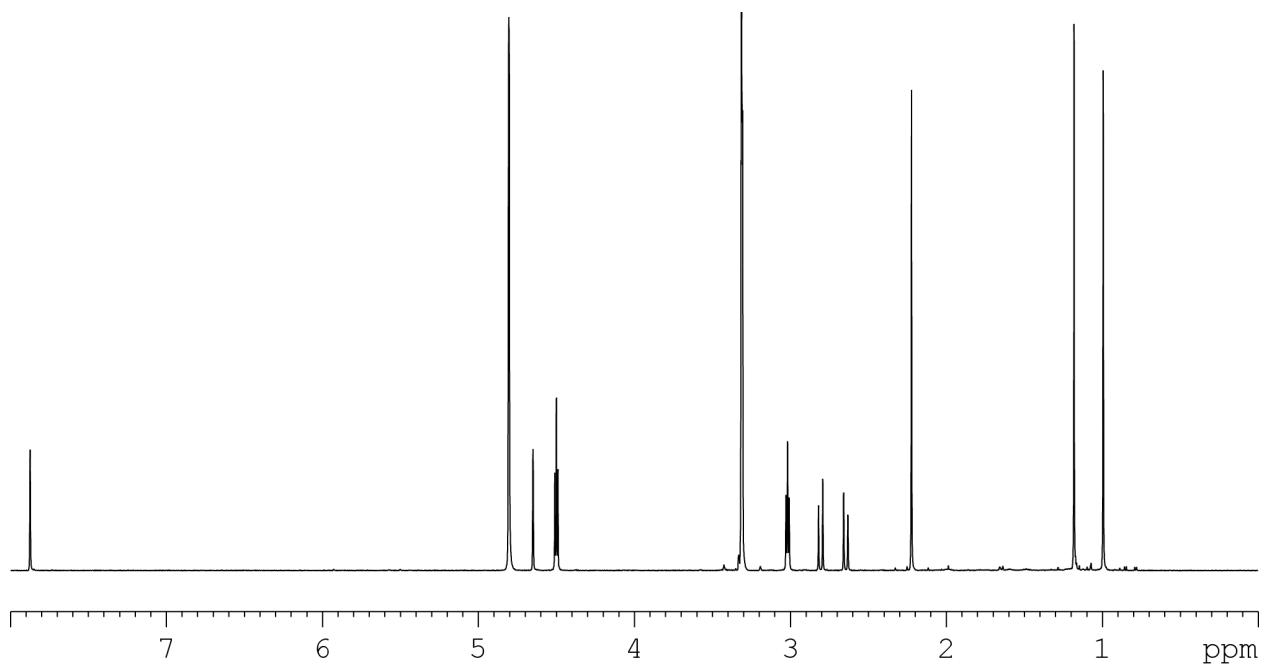
**Figure S9.**  $^1\text{H}$ -NMR (methanol- $d_4$ , 600 MHz) spectrum of echinolactone D.



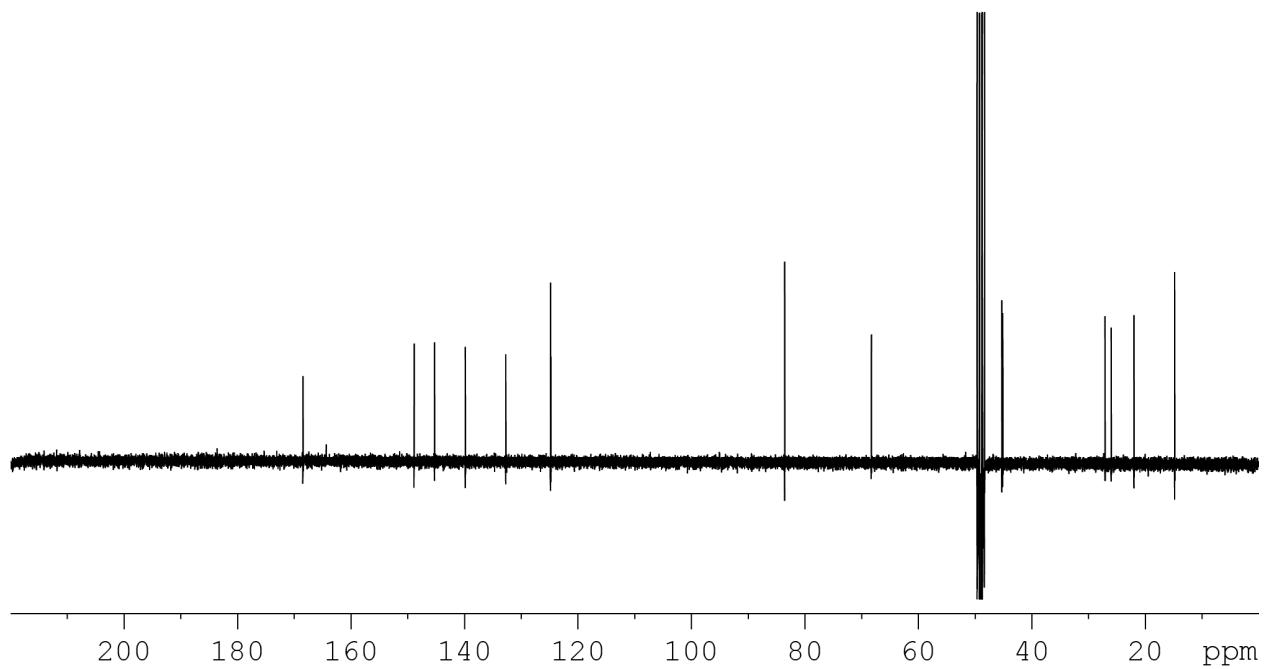
**Figure S10.**  $^{13}\text{C}$ -NMR (methanol- $d_4$ , 100 MHz) spectrum of echinolactone D.



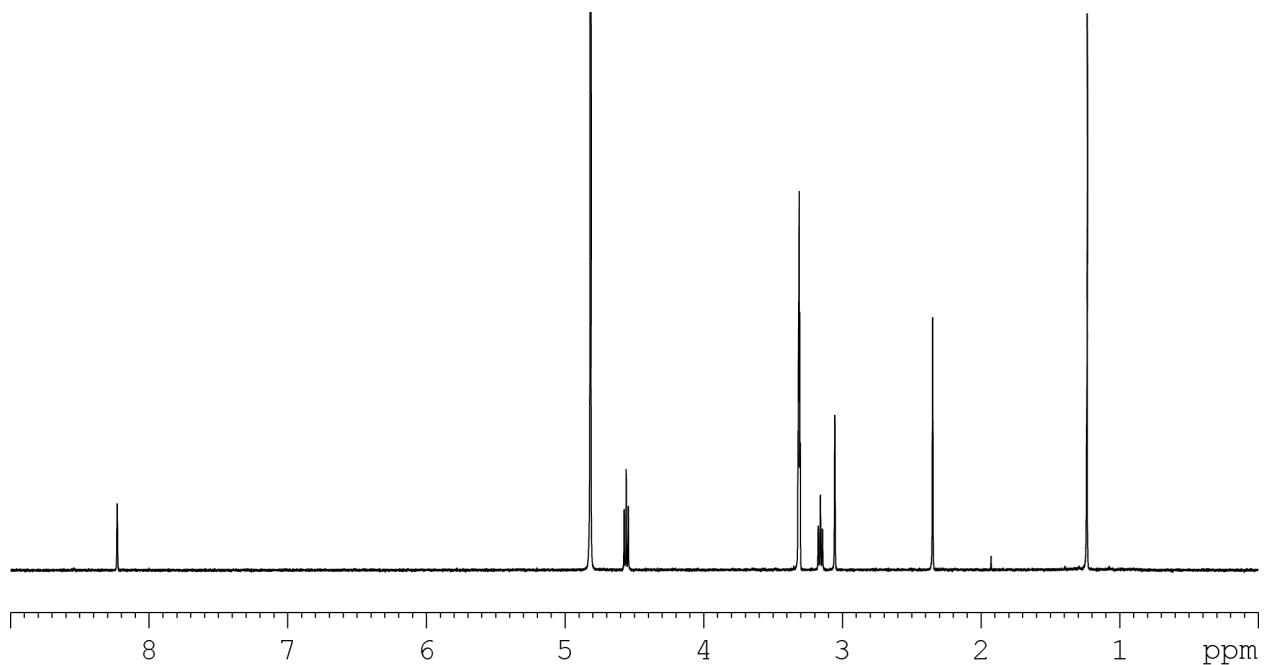
**Figure S11.**  $^1\text{H}$ -NMR (methanol- $d_4$ , 600 MHz) spectrum of radulactone.



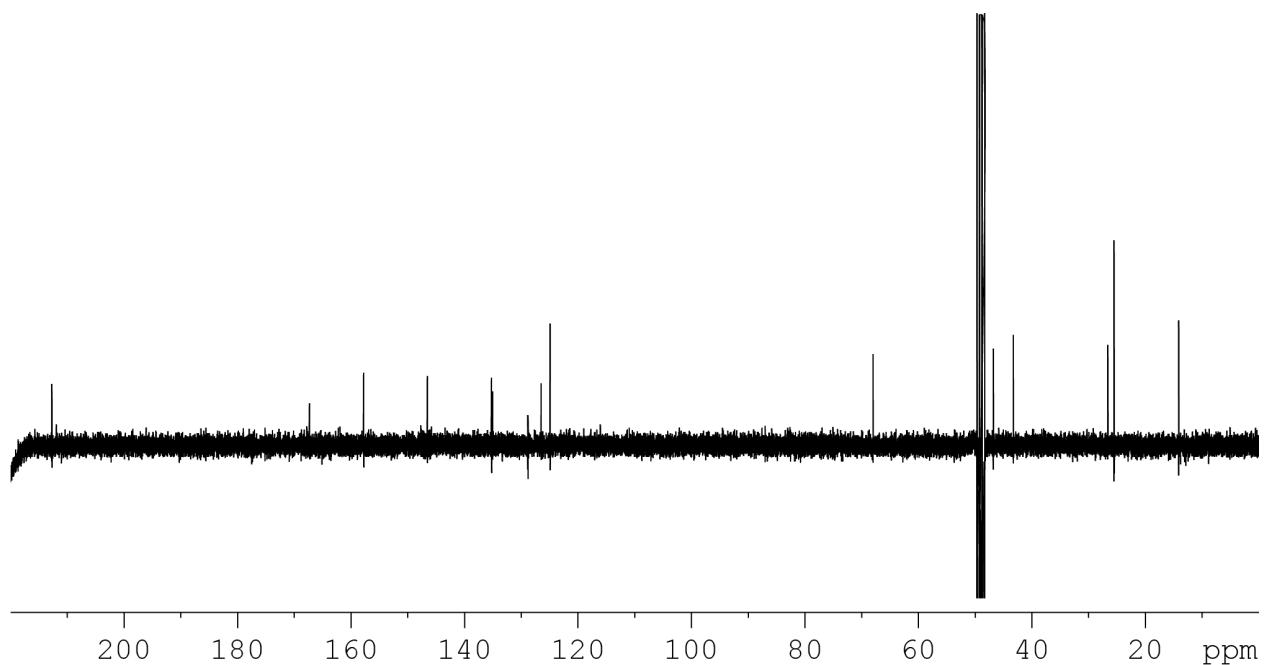
**Figure S12.**  $^{13}\text{C}$ -NMR (methanol- $d_4$ , 100 MHz) spectrum of radulactone.



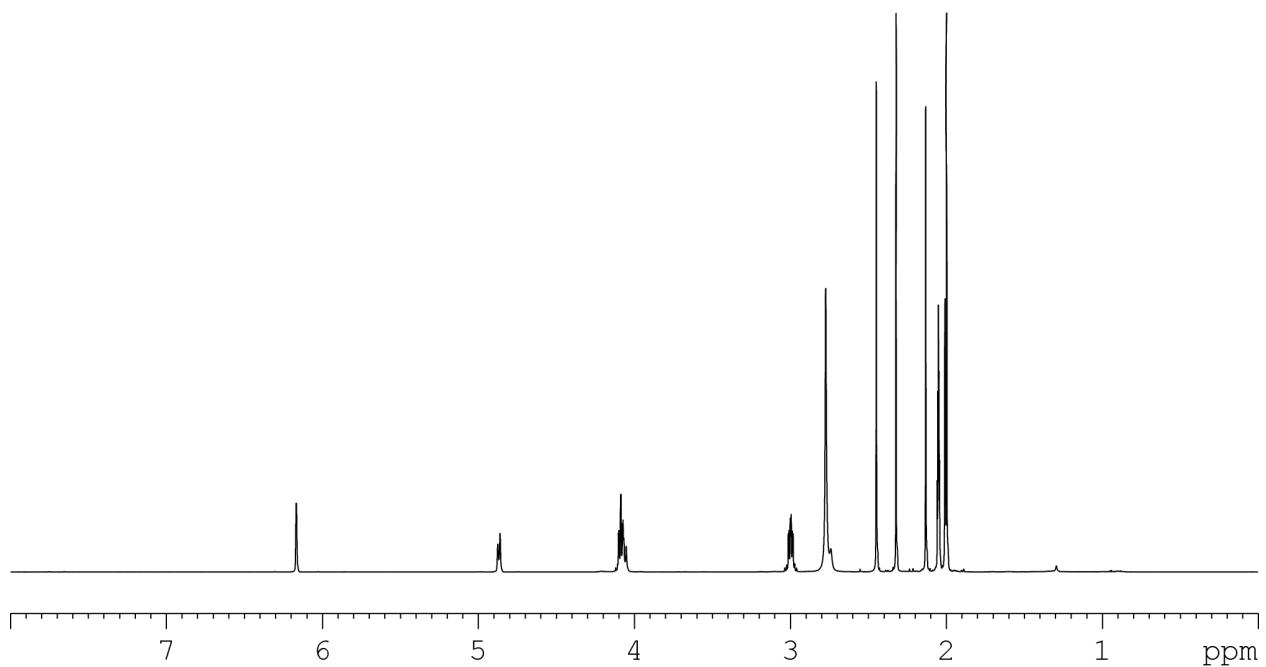
**Figure S13.**  $^1\text{H}$ -NMR (methanol- $d_4$ , 600 MHz) spectrum of echinolactone A.



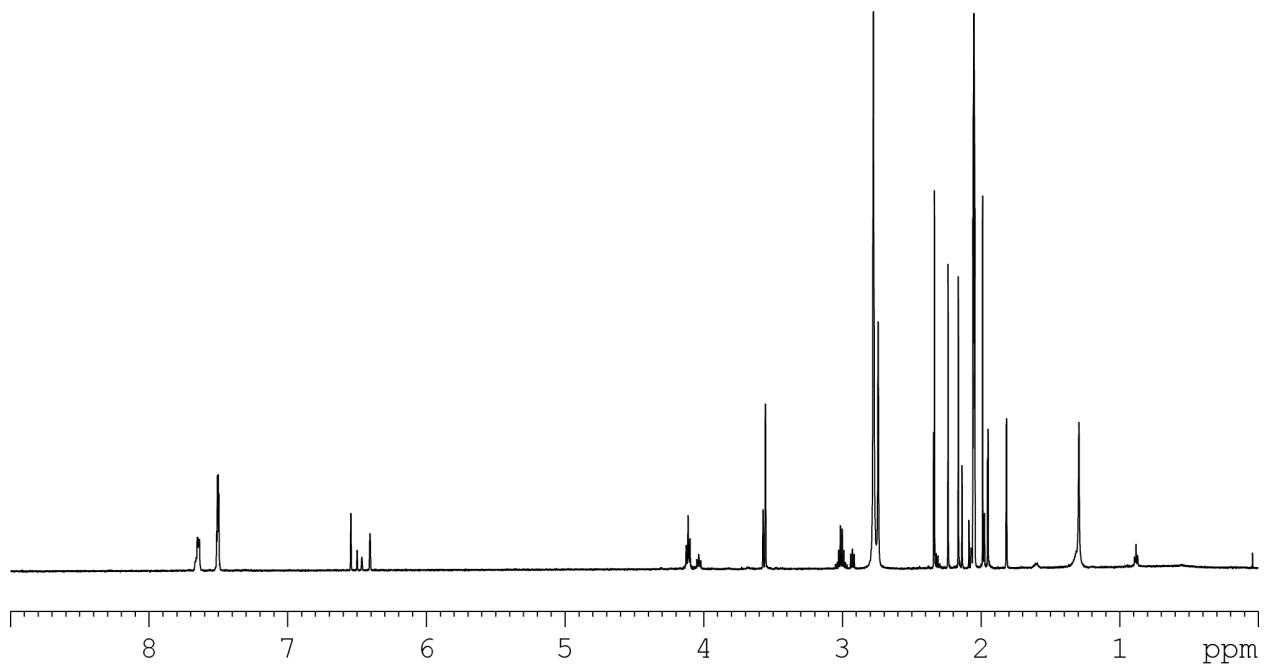
**Figure S14.**  $^{13}\text{C}$ -NMR (methanol- $d_4$ , 100 MHz) spectrum of echinolactone D.



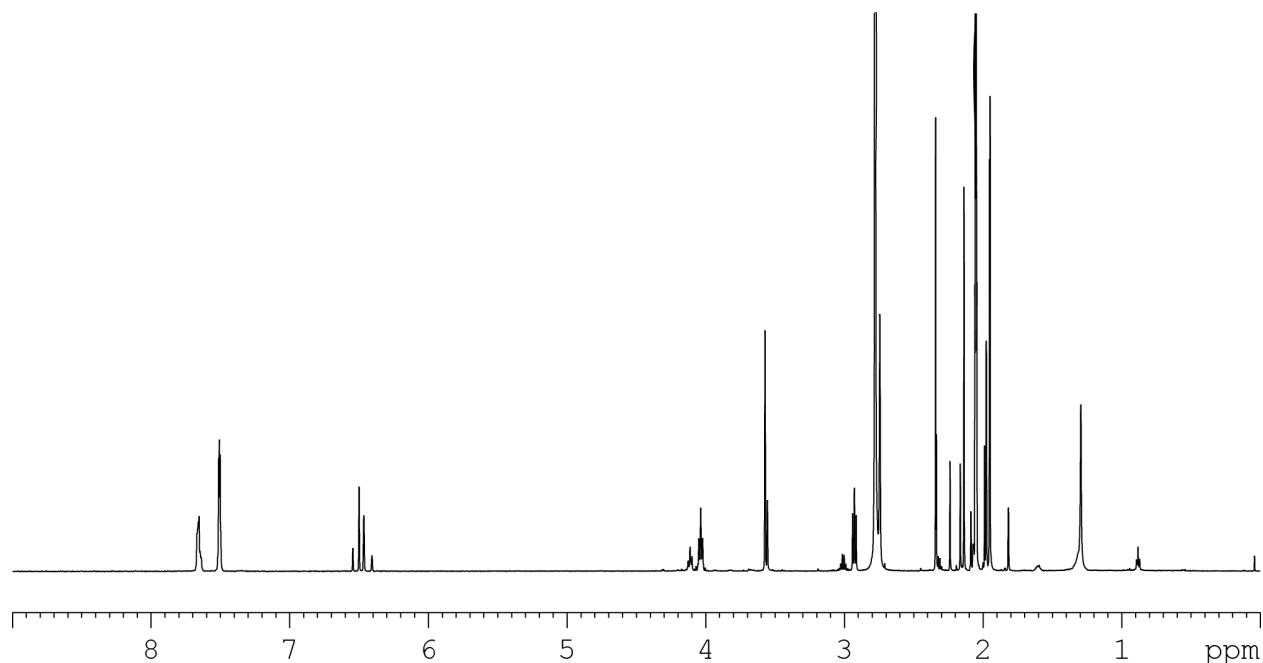
**Figure S15.**  $^1\text{H}$ -NMR (acetone- $d_6$ , 600 MHz) spectrum of **1a**.



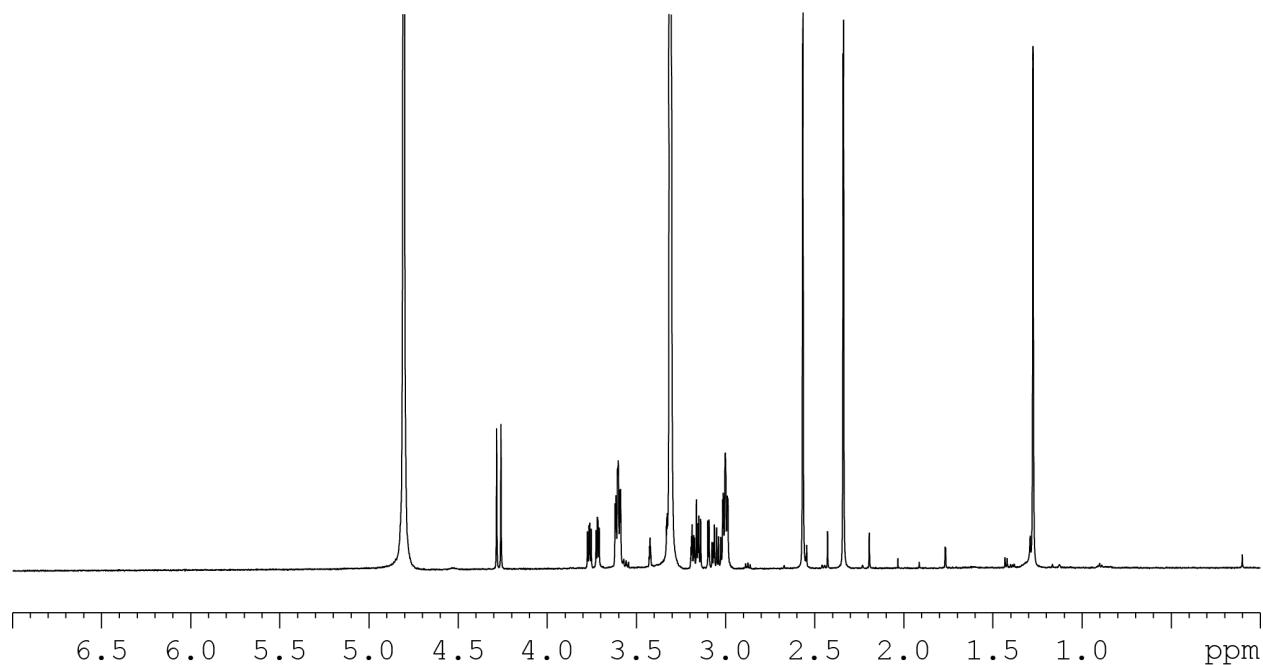
**Figure S16.**  $^1\text{H}$ -NMR (acetone- $d_6$ , 600 MHz) spectrum of the (S)-MTPA ester of **1a**.



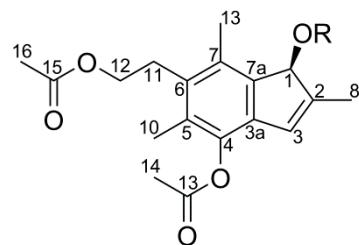
**Figure S17.**  $^1\text{H}$ -NMR (acetone- $d_6$ , 600 MHz) spectrum of the (R)-MTPA ester of **1a**.



**Figure S18.**  $^1\text{H}$ -NMR (methanol- $d_6$ , 600 MHz) spectrum of the reaction product of **3** and cysteine.



**Figure S19.** Structure of **1a** ( $\text{R} = \text{OH}$ ) and the R- and S-MTPA monoesters of **1a** ( $\text{R} = \text{R-MTPA}$  and  $\text{R} = \text{S-MTPA}$ , respectively).



**Table S1.**  $^1\text{H-NMR}$  data for compound **1a** and the R- and S-MTPA monoesters of **1a** (acetone- $d_6$ , 30 °C, 600 MHz).

pos.	<b>1a</b>	<b>R-MTPA Ester of 1a</b>	<b>S-MTPA Ester of 1a</b>
	$\delta_{\text{H}}$ (J in Hz)	$\delta_{\text{H}}$ (J in Hz)	$\delta_{\text{H}}$ (J in Hz)
<b>1</b>	4.87, m	6.47, s	6.54, s
<b>2</b>			
<b>3</b>	6.17, bs	6.5, s	6.41, s
<b>4</b>			
<b>4a</b>			
<b>5</b>			
<b>6</b>			
<b>7</b>			
<b>7a</b>			
<b>8</b>	2.01, bs	1.98, bs	1.82, s
<b>9</b>			
<b>10</b>	2.13, s	2.14, s	2.16, s
<b>11</b>	3.00, m	2.93, m	3.01, m
<b>12</b>	4.09, m	4.00, m	4.11, m
<b>13</b>	2.45, s	1.95, s	2.23, s
<b>14</b>	2.32, s	2.34, s	2.34, s
<b>15</b>			
<b>16</b>	2.00, s	1.95, s	1.99, s