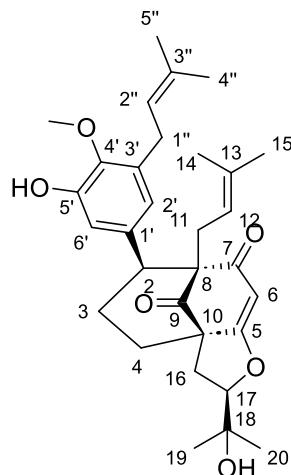
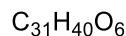


## Description of the Compound Isolated.

Compound **1** (Hymenotamayonin G): (2S,8R,10R,17R)-2-(5-hydroxy, 4-methoxy-3-(3-methylbut-2-en-1-yl)phenyl)-12-(2-hydroxypropan-2-yl)-8-(3-methylbut-2-en-1-yl)-5-oxotricyclo[6.3.1.0<sup>5,10</sup>]dodec-5-ene-7,9-dione. Amorphous pale yellow powder, HRESIMS *m/z* 509.2894 [M+H]<sup>+</sup> (calculated for C<sub>31</sub>H<sub>41</sub>O<sub>6</sub>, error -0.65 ppm); [α]<sub>D</sub><sup>20</sup> -16 (c 0.03, MeOH); UV (c 0.03, MeOH) λ<sub>max</sub> 220, 269 nm.



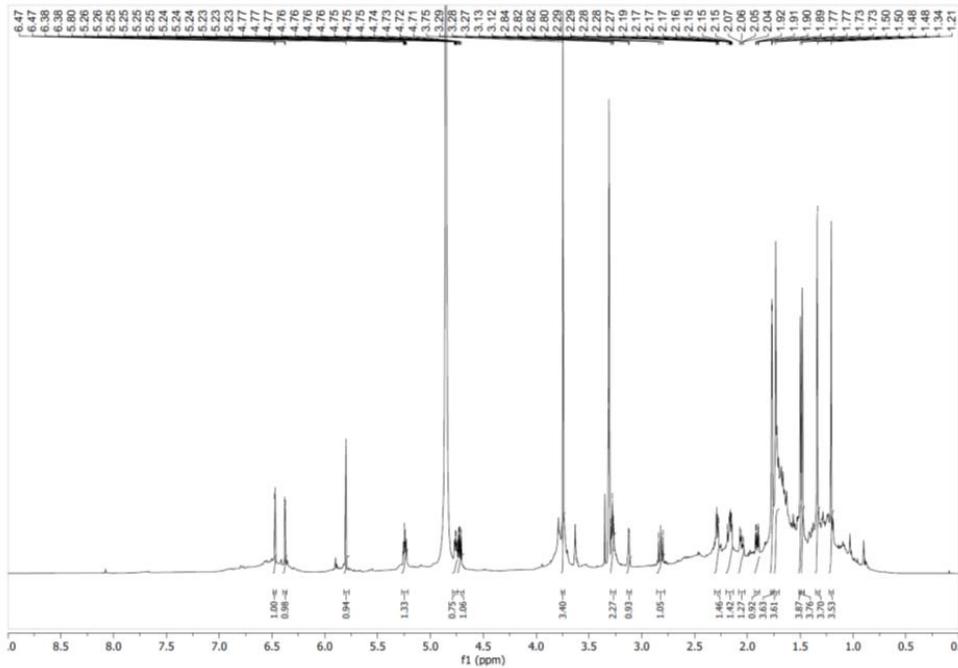
Chemical Formula:



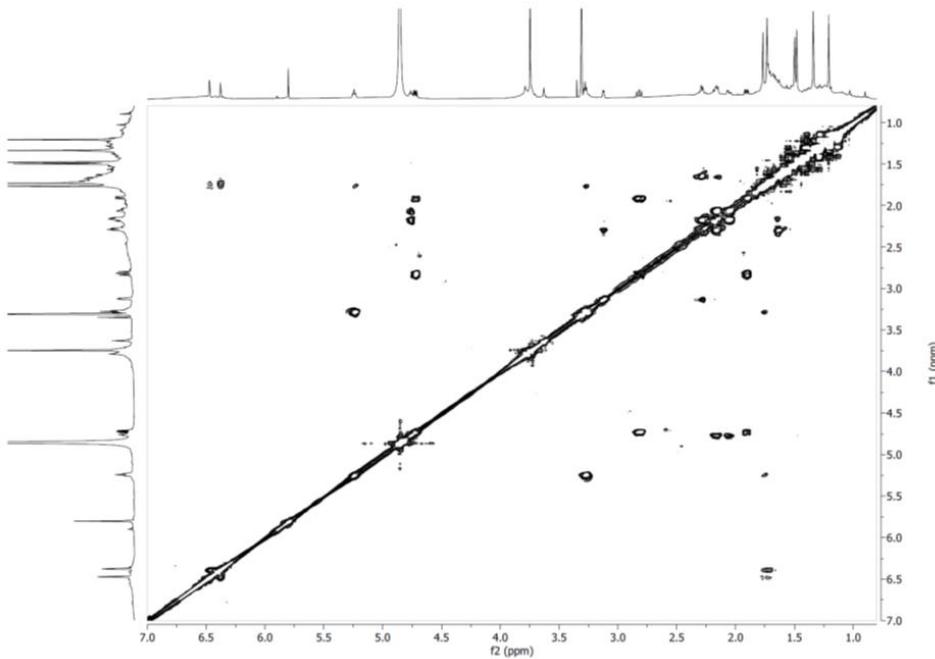
Exact Mass: 508.28

<sup>1</sup>H NMR (CD<sub>3</sub>OD, 600 MHz) δ 1.21 (3H, s, H<sub>3</sub>-20), 1.34 (3H, s, H<sub>3</sub>-19), 1.48 (3H, d, *J* = 1.2 Hz, H<sub>3</sub>-14), 1.50 (3H, d, *J* = 1.2 Hz, H<sub>3</sub>-15), 1.64 (1H, overlapped, H-3eq), 1.73 (3H, d, *J* = 1.3 Hz, H<sub>3</sub>-4''), 1.77 (3H, d, *J* = 1.3 Hz, H<sub>3</sub>-5''), 1.91 (1H, dd, *J* = 12.9, 5.5 Hz, H-16b), 2.05 (1H, dd, *J* = 14.3, 6.0 Hz, H-11b), 2.16 (1H, overlapped, H-4eq), 2.17 (1H, dd, *J* = 14.3, 7.9 Hz, H-11a), 2.28 (2H, m, H-3ax, H-4ax), 2.82 (1H, t, *J* = 12.9, 10.9 Hz, H-16a), 3.12 (1H, d, *J* = 5.4 Hz, H-2), 3.28 (2H, m, H<sub>2</sub>-1''), 3.75 (3H, s, 4'-OCH<sub>3</sub>), 4.72 (1H, dd, *J* = 10.9, 5.5 Hz, H-17), 4.76 (1H, thept, *J* = 7.9, 6.0, 1.2 Hz, H-12), 5.24 (1H, thept, *J* = 6.7, 1.3 Hz, H-2''), 5.80 (1H, s, H-6), 6.38 (1H, d, *J* = 2.3 Hz, H-2'), 6.47 (1H, d, *J* = 2.3 Hz, H-6'); <sup>13</sup>C NMR (CD<sub>3</sub>OD, 151 MHz) δ 17.9 (CH<sub>3</sub>-4''), 18.0 (CH<sub>3</sub>-14), 25.4 (CH<sub>3</sub>-20), 26.0 (CH<sub>3</sub>-5''), 26.1 (CH<sub>3</sub>-15), 26.5 (CH<sub>3</sub>-19), 27.5 (CH<sub>2</sub>-3), 29.1 (CH<sub>2</sub>-1''), 30.4 (CH<sub>2</sub>-11), 30.8 (CH<sub>2</sub>-16), 33.1 (CH<sub>2</sub>-4), 55.2 (CH-2), 60.8 (4'-OCH<sub>3</sub>), 61.7 (C-10), 67.2 (C-8), 71.1 (C-18), 92.8 (CH-17), 104.3 (CH-6), 115.8 (CH-6'), 121.1 (CH-12), 121.6 (CH-2'), 123.9 (CH-2''), 133.6 (C-3''), 134.1 (C-13), 136.3 (C-3'), 137.9 (C-1'), 146.0 (C-4'), 151.0 (C-5'), 181.2 (C-5), 201.3 (C-7), 207.7 (C-9)

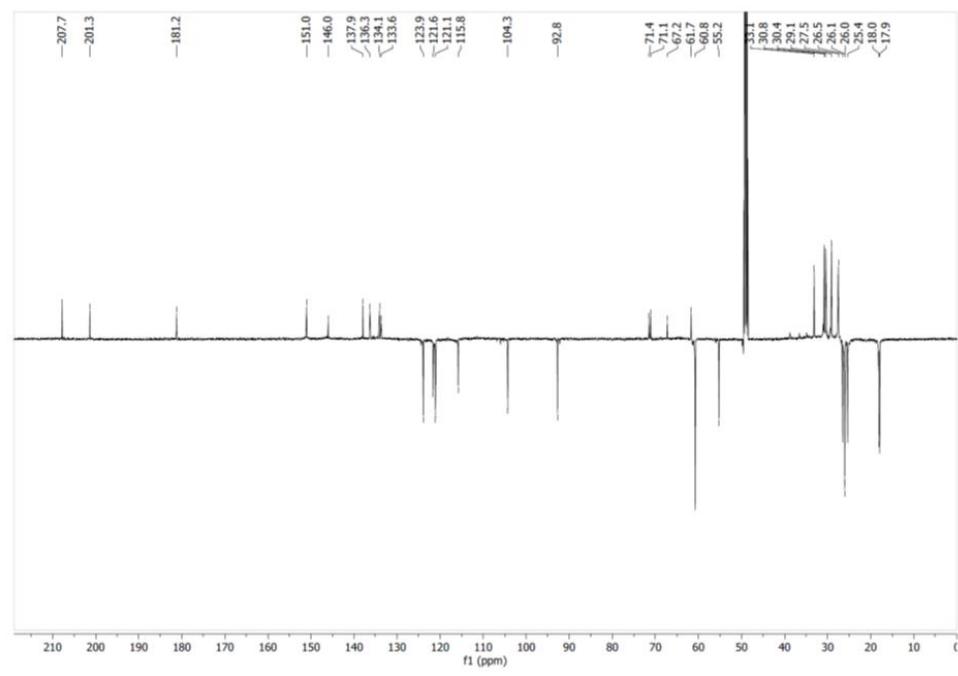
Supplementary Figures S5.2.6-S5.2.11



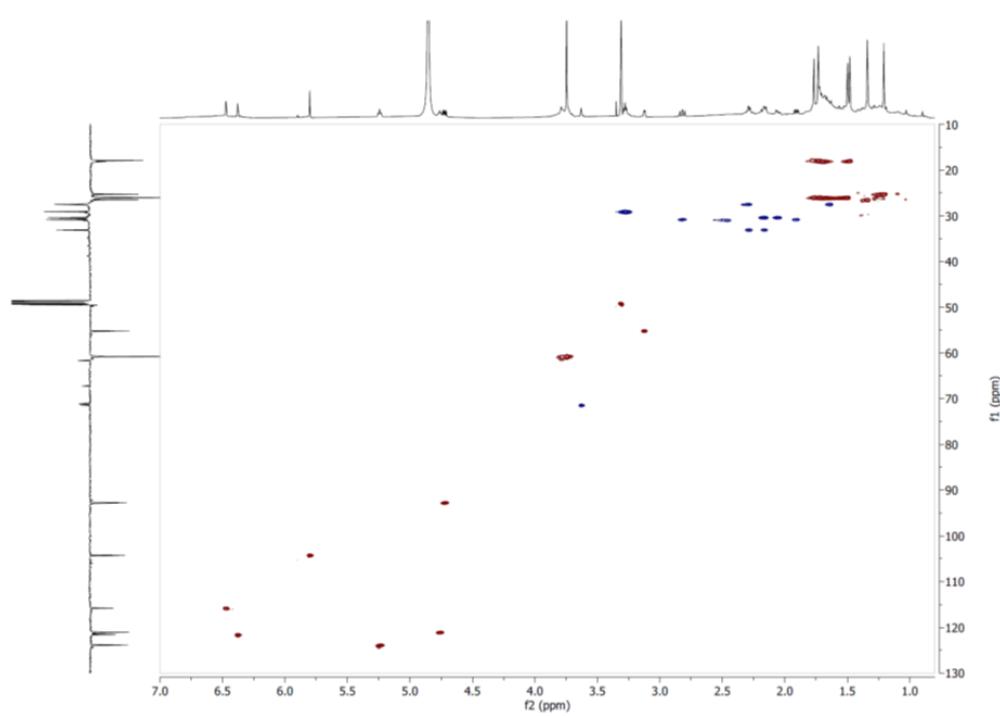
Supplementary Figure S5.2.6.  $^1\text{H}$  NMR spectrum of compound 1 in  $\text{CD}_3\text{OD}$  at 600 MHz



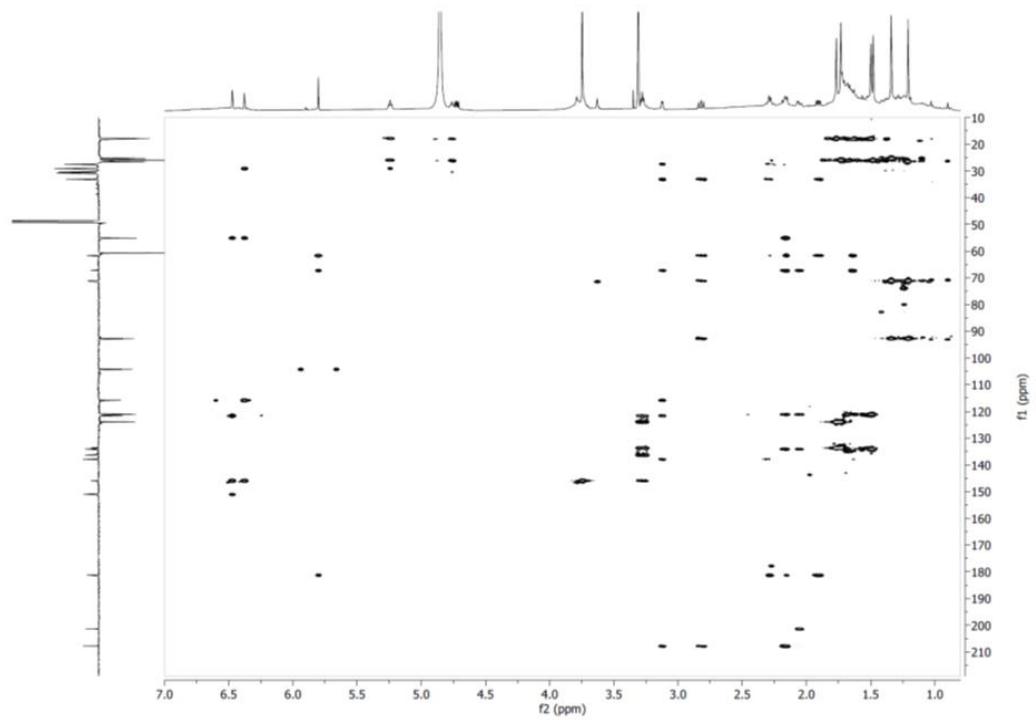
Supplementary Figure S5.2.7. COSY NMR spectrum of compound 1 in CD<sub>3</sub>OD



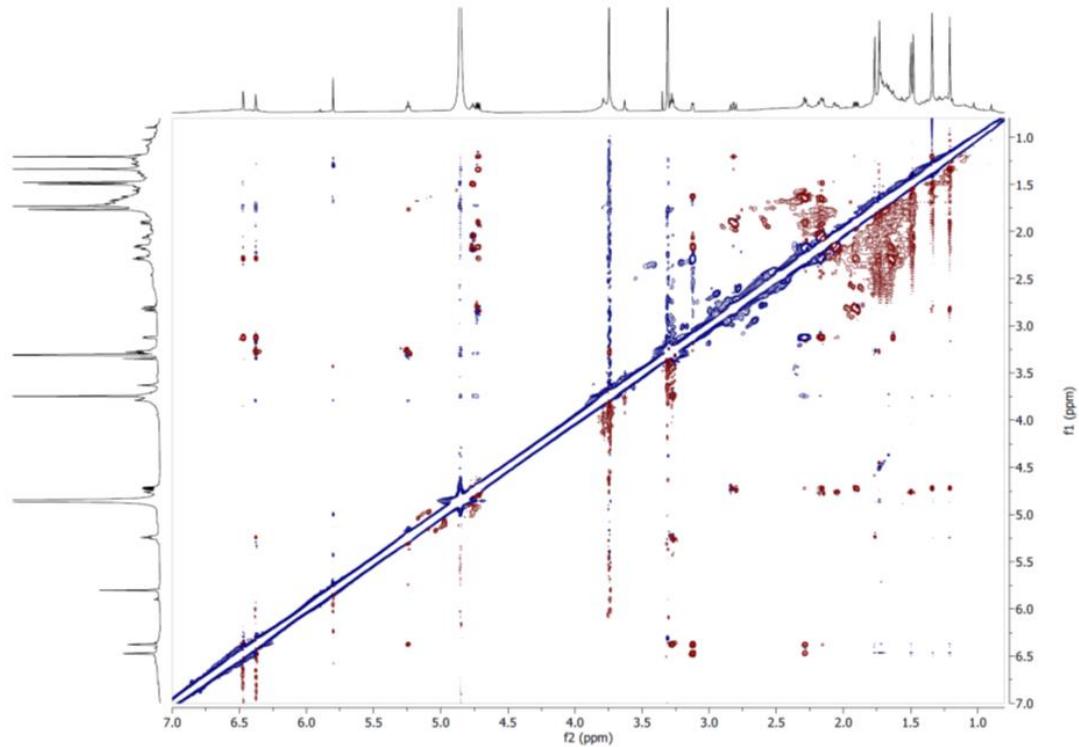
Supplementary Figure S5.2.8.  $^{13}\text{C}$ -DEPTQ NMR spectrum of compound 1 in  $\text{CD}_3\text{OD}$  at 151 MHz



Supplementary Figure S5.2.9. Edited HSQC NMR spectrum of compound 1 in  $\text{CD}_3\text{OD}$

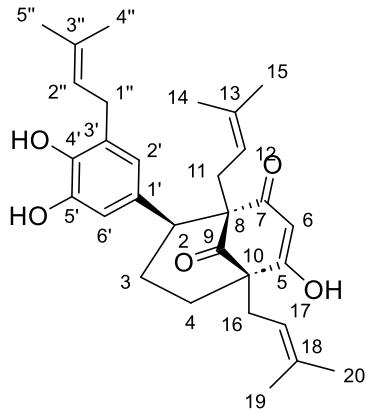


Supplementary Figure S5.2.10. HMBC NMR spectrum of compound 1 in  $\text{CD}_3\text{OD}$



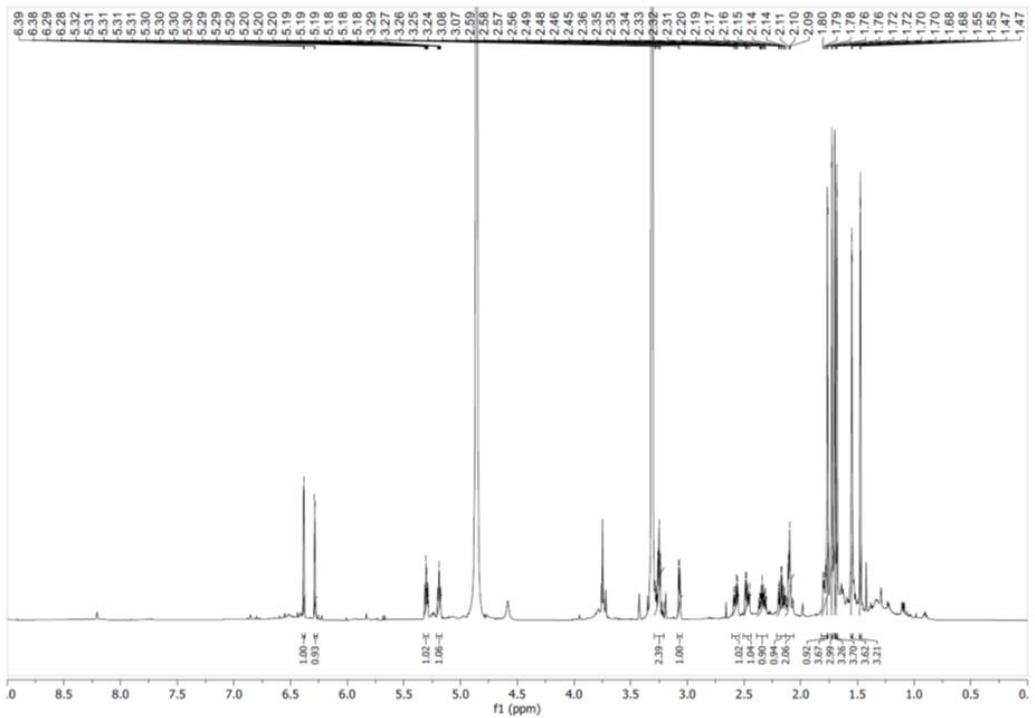
Supplementary Figure S5.2.11. ROESY NMR spectrum of compound 1 in  $\text{CD}_3\text{OD}$

Compound **2** (Hymenotamayonin A): (*2S,8R,10R*)-2-(4,5-dihydroxy-3-(3-methylbut-2-en-1-yl)phenyl)-5-hydroxy-8,10-bis(3-methylbut-2-en-1-yl)bicyclo[3.3.1]non-6-ene-7,9-dione. Amorphous pale yellow powder, HRESIMS *m/z* 479.2793 [M+H]<sup>+</sup> (calculated for C<sub>30</sub>H<sub>39</sub>O<sub>5</sub>, error 0.21 ppm); [α]<sub>D</sub><sup>20</sup> -2 (c 0.001, MeOH); UV (c 0.001, MeOH) λ<sub>max</sub> 213, 281 nm.

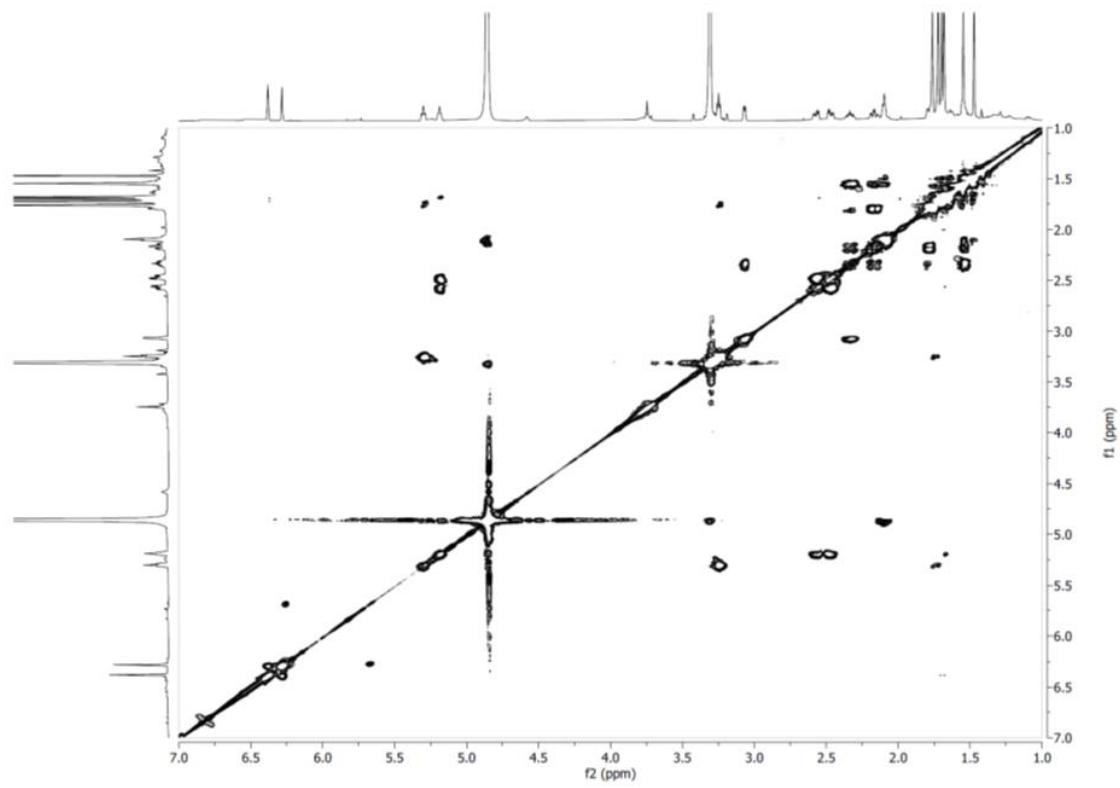


Chemical Formula: C<sub>30</sub>H<sub>38</sub>O<sub>5</sub>  
Exact Mass: 478.27

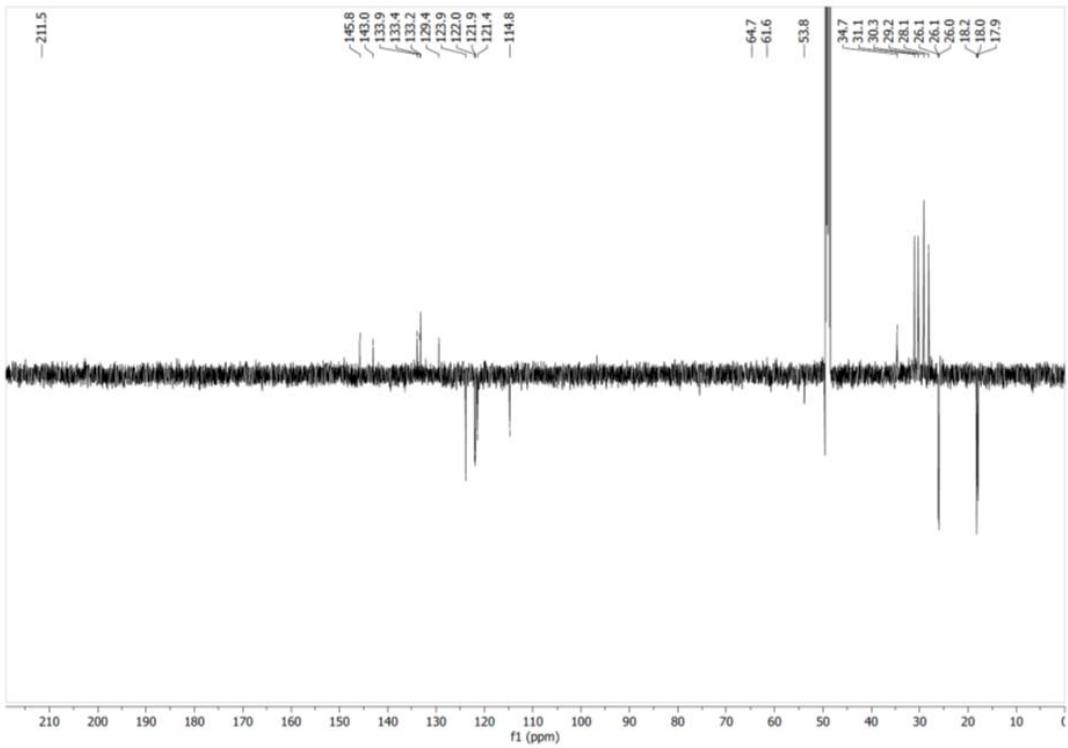
<sup>1</sup>H NMR (CD<sub>3</sub>OD, 600 MHz) δ 1.47 (3H, d, *J* = 1.5 Hz, H<sub>3</sub>-14), 1.55 (3H, d, *J* = 1.5 Hz, H<sub>3</sub>-15), 1.55 (1H, overlapped, H-3eq), 1.68 (3H, d, *J* = 1.5 Hz, H<sub>3</sub>-20), 1.70 (3H, d, *J* = 1.5 Hz, H<sub>3</sub>-19), 1.72 (3H, d, *J* = 1.4 Hz, H<sub>3</sub>-4''), 1.76 (3H, d, *J* = 1.4 Hz, H<sub>3</sub>-5''), 1.79 (1H, dd, *J* = 13.8, 5.2 Hz, H-4eq), 2.09 (2H, m, H<sub>2</sub>-11), 2.17 (1H, td, *J* = 13.8, 4.9 Hz, H-4ax), 2.34 (1H, tt, *J* = 14.3, 5.8 Hz, H-3ax), 2.47 (1H, dd, *J* = 14.5, 6.9 Hz, H-16b), 2.57 (1H, dd, *J* = 14.5, 6.9 Hz, H-16a), 3.07 (1H, d, *J* = 6.4 Hz, H-2eq), 3.25 (2H, m, H<sub>2</sub>-1''), 4.87 (1H, overlapped, H-12), 5.19 (1H, thept, *J* = 6.9, 1.5 Hz, H-17), 5.30 (1H, thept, *J* = 7.4, 1.4 Hz, H-2''), 6.28 (1H, d, *J* = 2.2 Hz, H-2'), 6.38 (1H, d, *J* = 2.2 Hz, H-6'); <sup>13</sup>C NMR (CD<sub>3</sub>OD, 151 MHz) δ 17.9 (CH<sub>3</sub>-4''), 18.0 (CH<sub>3</sub>-14), 18.2 (CH<sub>3</sub>-19), 26.0 (CH<sub>3</sub>-5''), 26.1 (CH<sub>3</sub>-15), 26.1 (CH<sub>3</sub>-20), 28.1 (CH<sub>2</sub>-3), 29.2 (CH<sub>2</sub>-1''), 30.3 (CH<sub>2</sub>-11), 31.1 (CH<sub>2</sub>-16), 34.7 (CH<sub>2</sub>-4), 53.8 (CH-2), 61.6 (C-10), 64.7 (C-8), 114.8 (CH-6'), 121.4 (CH-2'), 121.9 (CH-17), 122.0 (CH-12), 123.9 (CH-2''), 129.4 (C-3'), 133.2 (C-3'', C-13), 133.4 (C-1'), 133.9 (C-18), 143.0 (C-4'), 145.8 (C-5'), 211.5 (C-9). Supplementary Figures S5.2.12–S5.2.17.



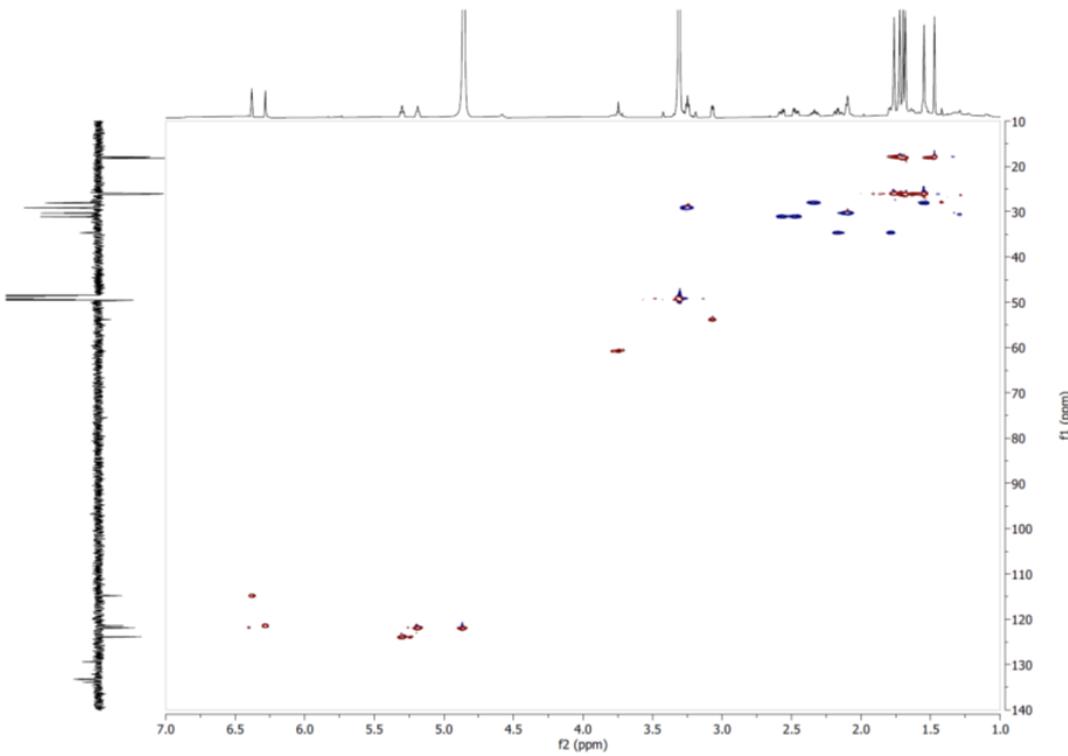
Supplementary Figure S5.2.12.  $^1\text{H}$  NMR spectrum of compound 2 in  $\text{CD}_3\text{OD}$  at 600 MHz



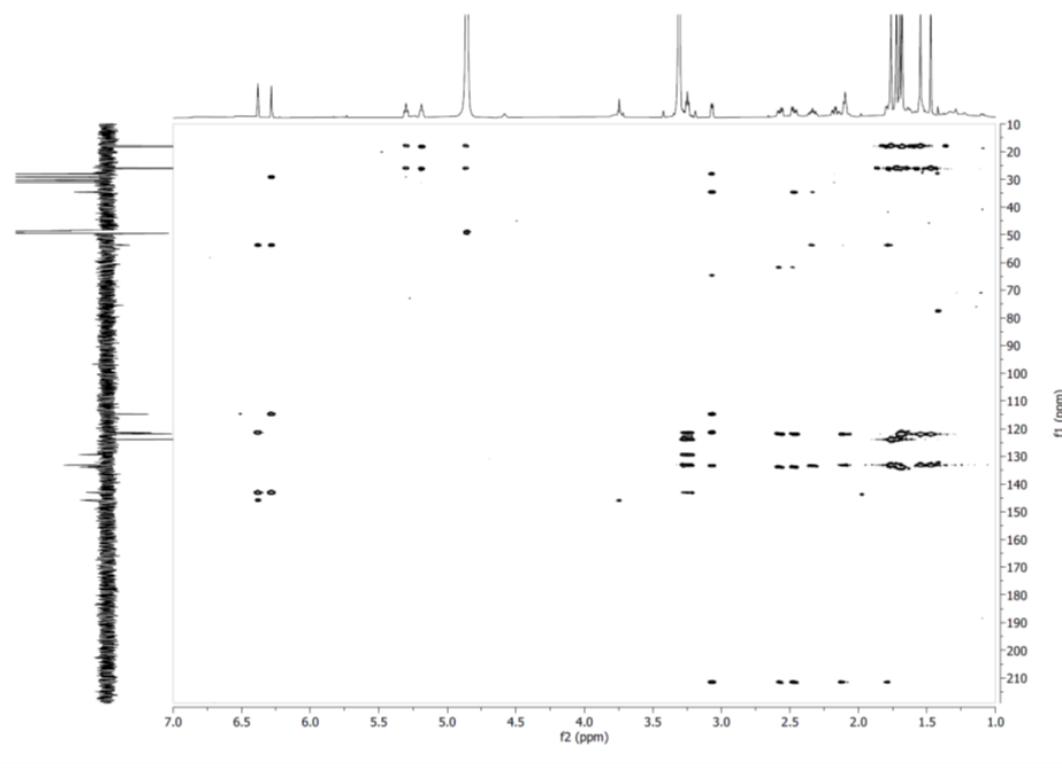
Supplementary Figure S5.2.13. COSY NMR spectrum of compound 2 in  $\text{CD}_3\text{OD}$



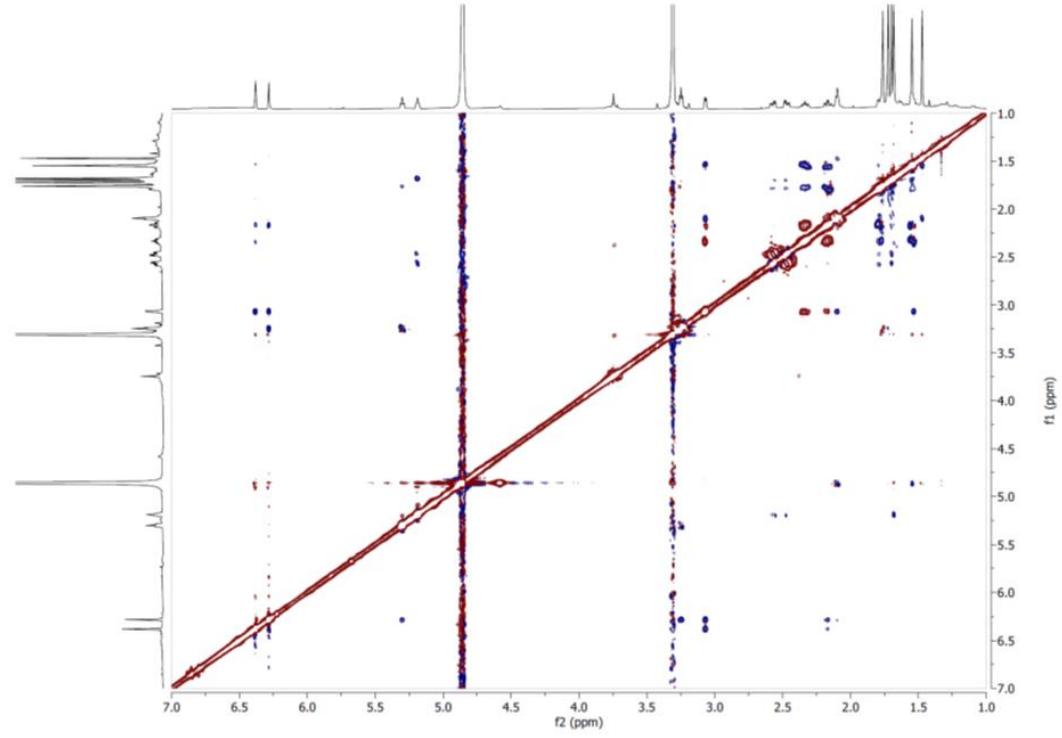
Supplementary Figure S5.2.14.  $^{13}\text{C}$ -DEPTQ NMR spectrum of compound 2 in  $\text{CD}_3\text{OD}$  at 151 MHz



Supplementary Figure S5.2.15. Edited HSQC NMR spectrum of compound 2 in  $\text{CD}_3\text{OD}$

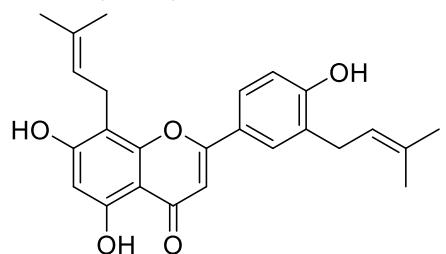


Supplementary Figure S5.2.16. HMBC NMR spectrum of compound 2 in  $\text{CD}_3\text{OD}$



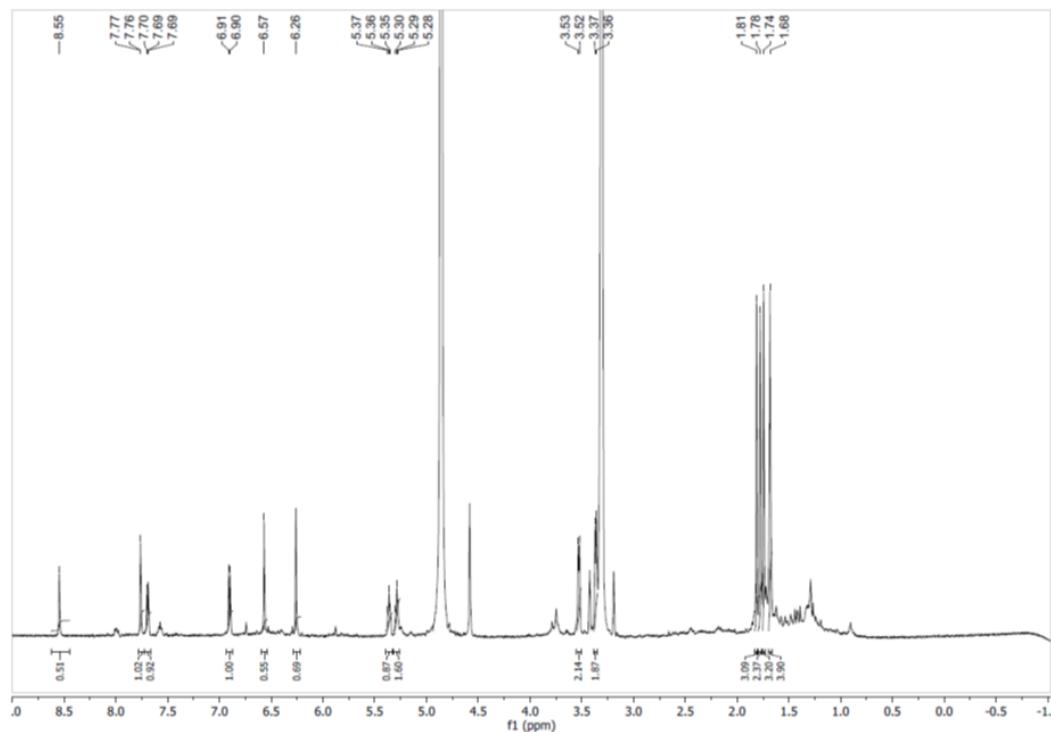
Supplementary Figure S5.2.17. ROESY NMR spectrum of compound 2 in  $\text{CD}_3\text{OD}$

Compound **3**: 3',8-diprenylapigenin [24]. Amorphous white powder, HRESIMS  $m/z$  407.1853  $[M+H]^+$  (calculated for  $C_{25}H_{39}O_5$ , error 0.14 ppm);  $[\alpha]_D^{20}$  -14 (c 0.0006, MeOH); UV (c 0.0006, MeOH)  $\lambda_{max}$  203, 276, 349 nm.

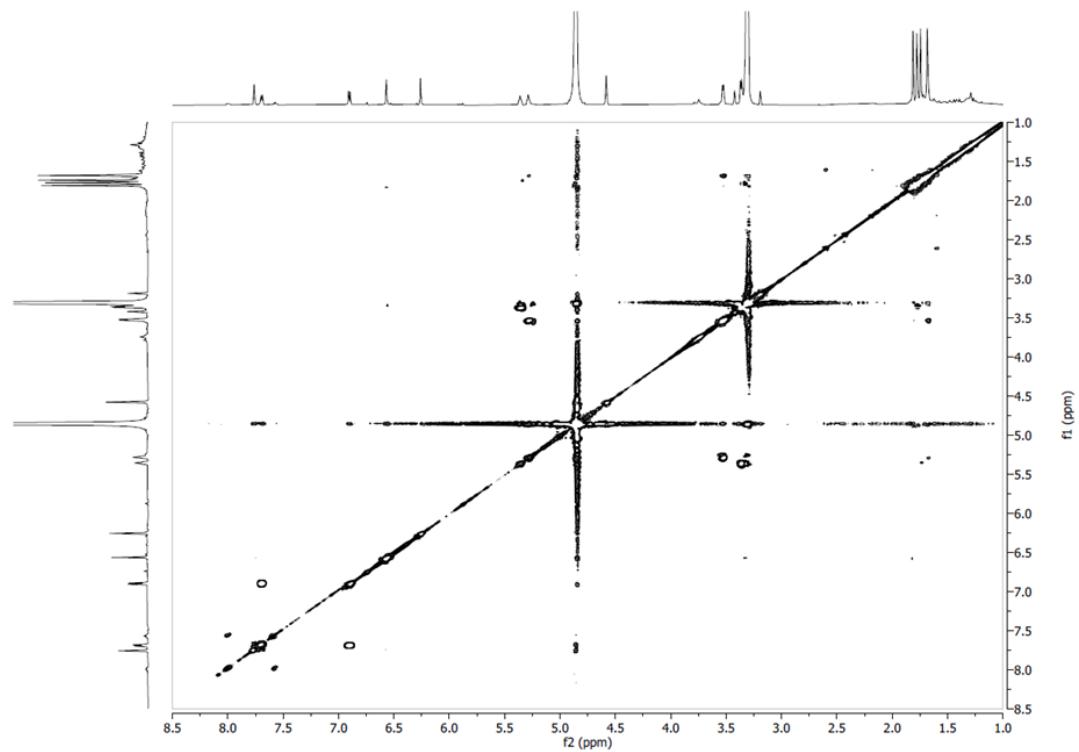


Chemical Formula: C<sub>25</sub>H<sub>26</sub>O<sub>5</sub>  
Exact Mass: 406.18

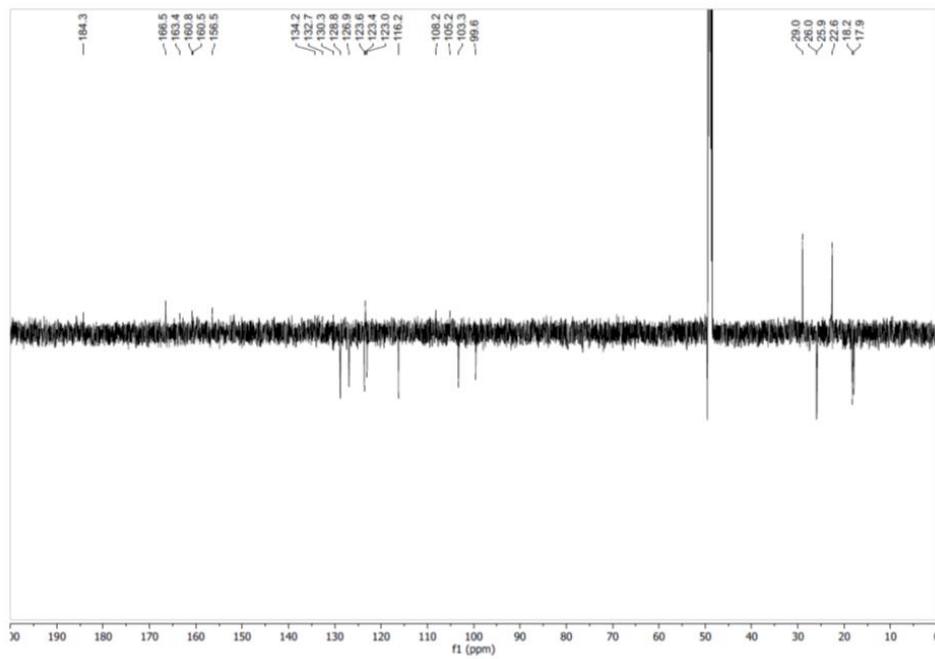
<sup>1</sup>H NMR (CD<sub>3</sub>OD, 600 MHz) δ 1.68 (3H, s, H<sub>3</sub>-5''), 1.74 (3H, s, H<sub>3</sub>-10''), 1.78 (3H, s, H<sub>3</sub>-11''), 1.81 (3H, s, H<sub>3</sub>-4''), 3.37 (2H, d, *J* = 7.4 Hz, H<sub>2</sub>-7''), 3.53 (2H, d, *J* = 7.2 Hz, H<sub>2</sub>-1''), 5.29 (1H, t, *J* = 7.2 Hz, H-2''); <sup>13</sup>C NMR (CD<sub>3</sub>OD, 151 MHz) δ 17.9 (CH<sub>3</sub>-10''), 18.2 (CH<sub>3</sub>-4''), 22.6 (CH<sub>2</sub>-1''), 25.9 (CH<sub>3</sub>-11''), 26.0 (CH<sub>3</sub>-5''), 29.0 (CH<sub>2</sub>-7''), 99.6 (CH-6), 103.3 (CH-3), 105.2 (C-10), 108.2 (C-8), 116.2 (CH-5''), 123.0 (CH-8''), 123.4 (C-1''), 123.6 (CH-2''), 126.9 (CH-6''), 128.8 (CH-2''), 130.3 (C-3''), 132.7 (C-3''), 134.2 (C-9''), 156.5 (C-9), 160.5 (C-4''), 160.8 (C-5), 163.4 (C-7), 166.5 (C-2), 184.3 (C-4). Supplementary Figures S5.2.18-S5.2.23.



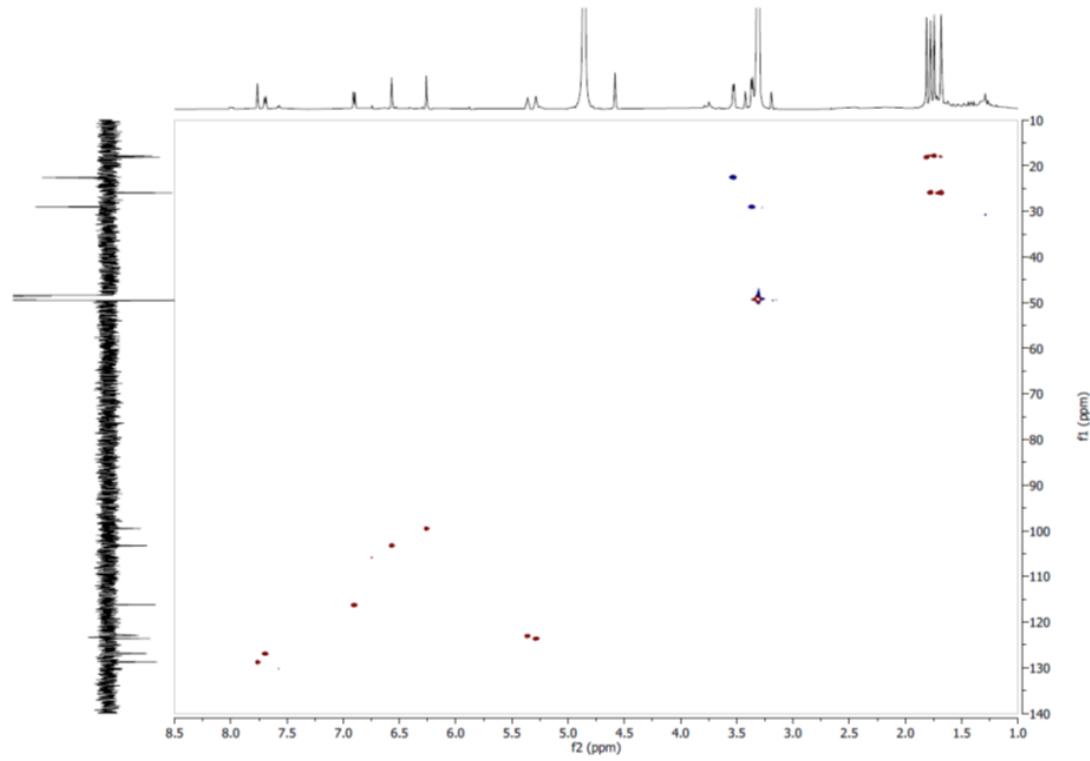
Supplementary Figure S5.2.18.  $^1\text{H}$  NMR spectrum of compound 3 in  $\text{CD}_3\text{OD}$  at 600 MHz



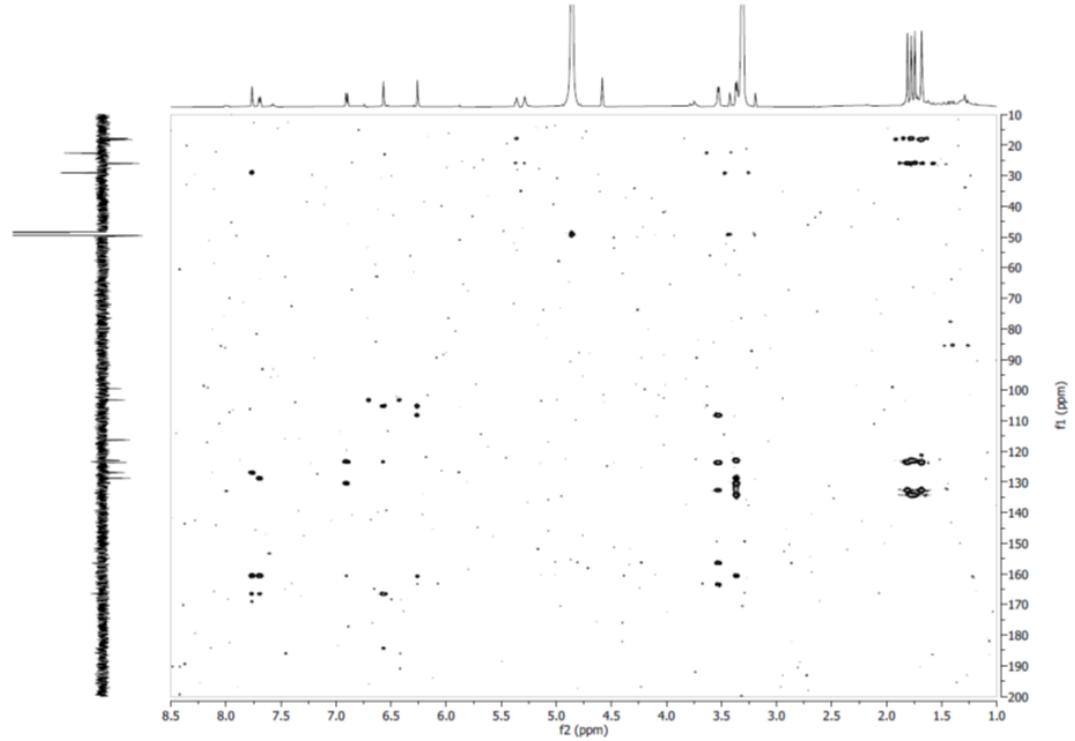
Supplementary Figure S5.2.19. COSY NMR spectrum of compound 3 in  $\text{CD}_3\text{OD}$



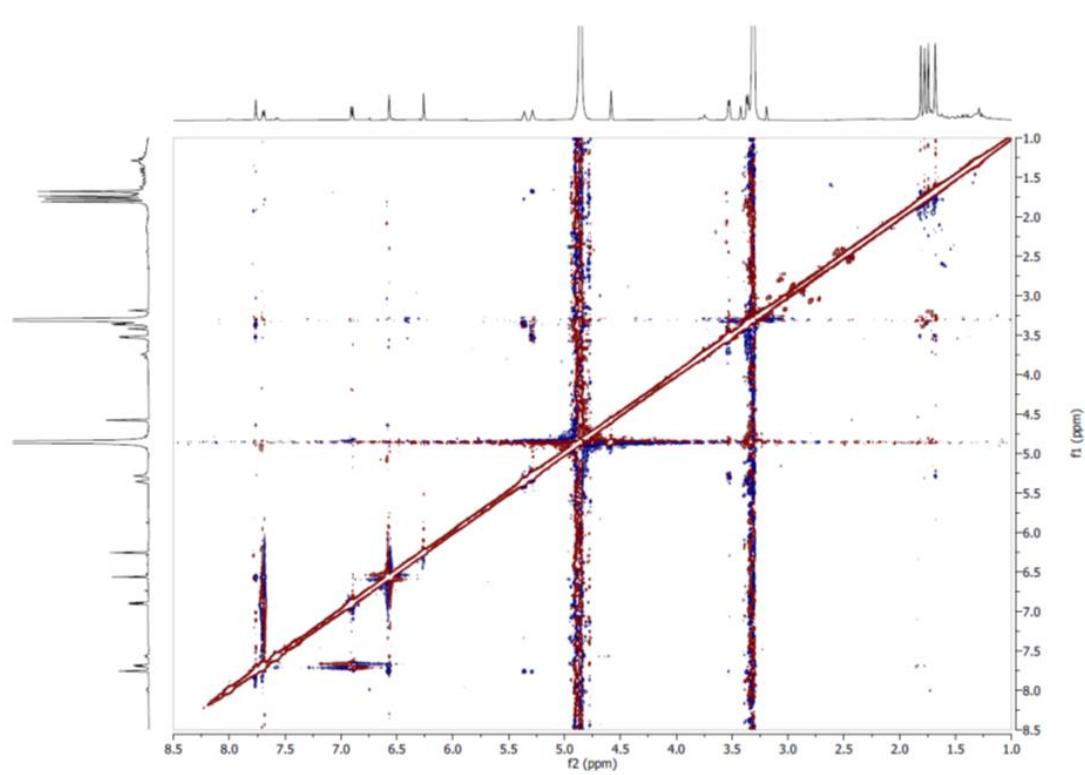
Supplementary Figure S5.2.20.  $^{13}\text{C}$ -DEPTQ NMR spectrum of compound 3 in  $\text{CD}_3\text{OD}$  at 151 MHz



Supplementary Figure S5.2.21. Edited HSQC NMR spectrum of compound 3 in  $\text{CD}_3\text{OD}$

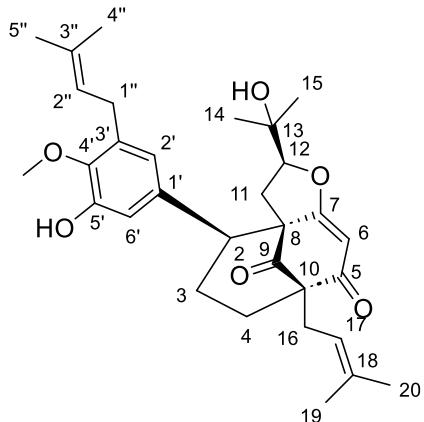


Supplementary Figure S5.2.22. HMBC NMR spectrum of compound 3 in  $\text{CD}_3\text{OD}$



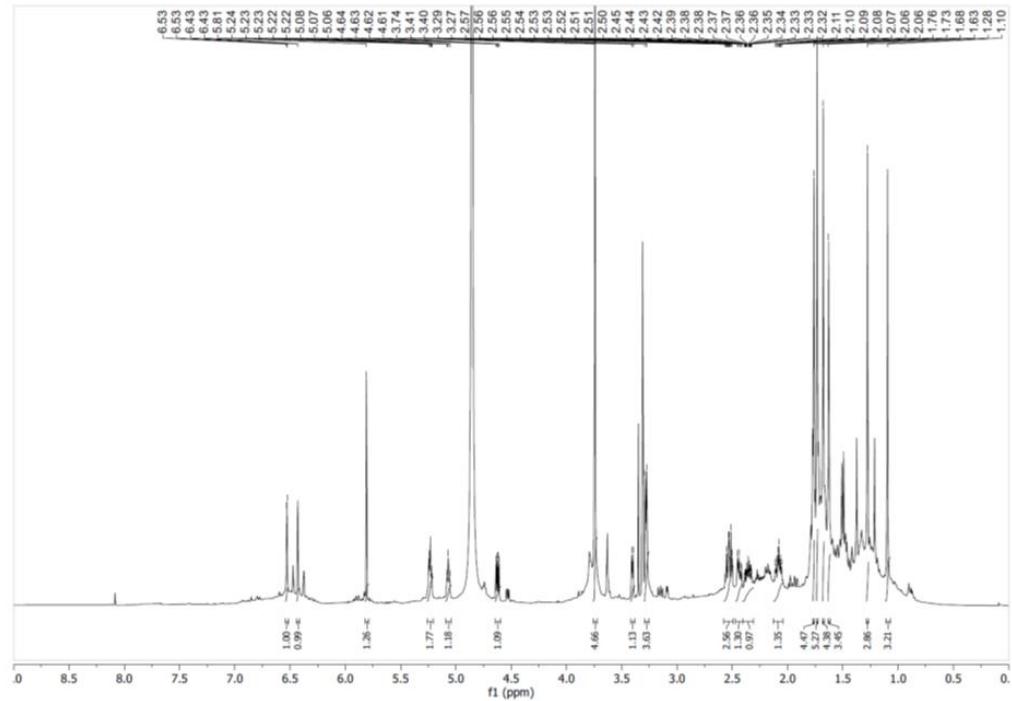
Supplementary Figure S5.2.23. ROESY NMR spectrum of compound 3 in  $\text{CD}_3\text{OD}$

Compound **4** (Hymenotamayonin H): (*2S,8R,10R,12S*)-2-(5-hydroxy, 4-methoxy-3-(3-methylbut-2-en-1-yl)phenyl)-17-(2-hydroxypropan-2-yl)-10-(3-methylbut-2-en-1-yl)-7-oxotricyclo[6.3.1.0<sup>7,8</sup>]dodec-6-ene-5,9-dione. Amorphous pale yellow powder, HRESIMS *m/z* 509.2894 [M+H]<sup>+</sup> (calculated for C<sub>31</sub>H<sub>41</sub>O<sub>6</sub>, error -0.65 ppm);  $[\alpha]_D^{20} +3$  (c 0.03, MeOH); UV (c 0.03, MeOH)  $\lambda_{\text{max}}$  214, 269 nm.

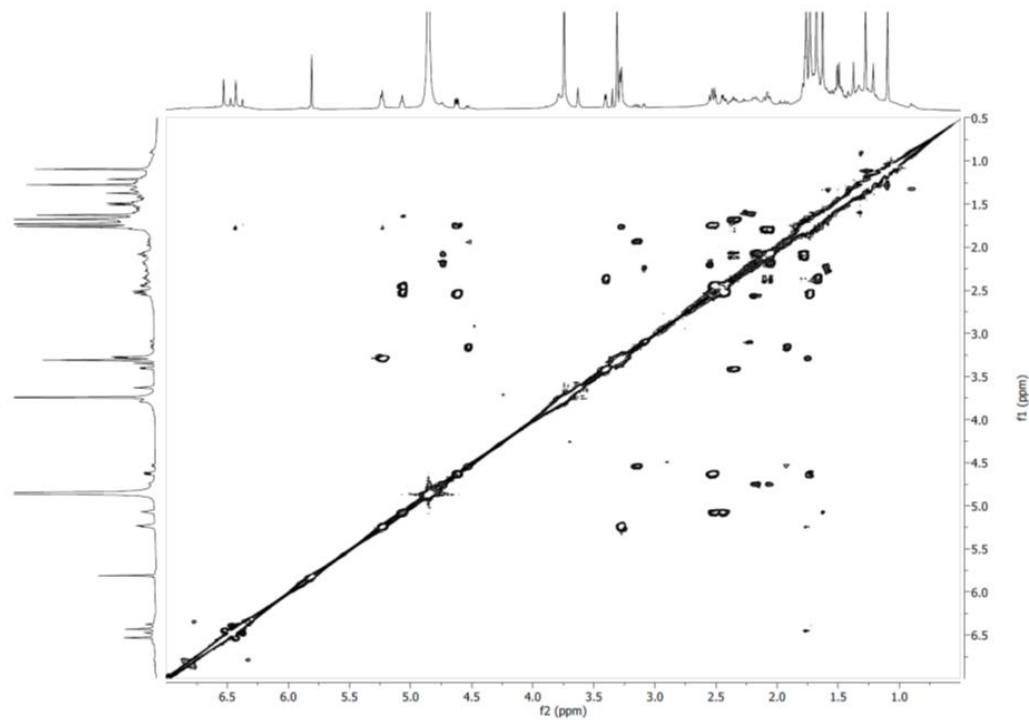


Chemical Formula: C<sub>31</sub>H<sub>40</sub>O<sub>6</sub>  
Exact Mass: 508.28

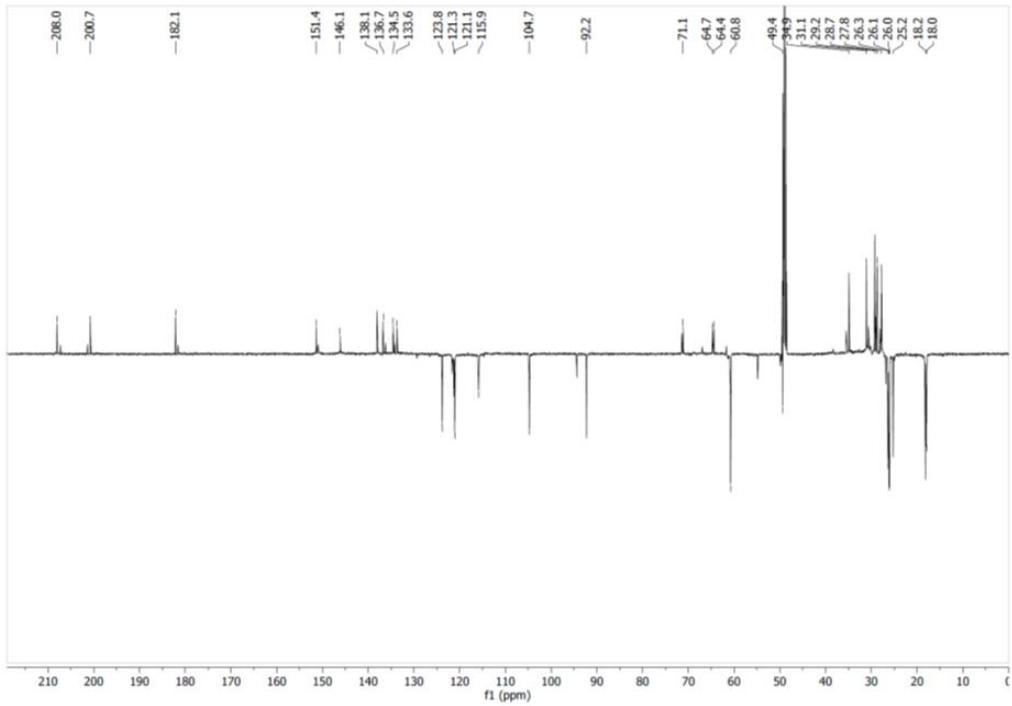
<sup>1</sup>H NMR (CD<sub>3</sub>OD, 600 MHz)  $\delta$  1.10 (3H, s, H<sub>3</sub>-15), 1.28 (3H, s, H<sub>3</sub>-14), 1.63 (3H, s, H<sub>3</sub>-20), 1.67 (1H, overlapped, H-3eq), 1.68 (3H, s, H<sub>3</sub>-19), 1.73 (3H, s, H<sub>3</sub>-4''), 1.74 (1H, overlapped, H-11b), 1.76 (3H, s, H<sub>3</sub>-5''), 1.78 (1H, overlapped, H-4eq), 2.08 (1H, td, *J* = 14.1, 4.8 Hz, H-4ax), 2.36 (1H, tt, *J* = 15.0, 14.1, 6.4, 5.0 Hz, H-3ax), 2.43 (1H, dd, *J* = 14.5, 6.9 Hz, H-16b), 2.53 (2H, m, H-11a, H-16a), 3.28 (2H, d, *J* = 7.4 Hz, H<sub>2</sub>-1''), 3.40 (1H, d, *J* = 6.4 Hz, H-2), 3.74 (3H, s, 4'-OCH<sub>3</sub>), 4.62 (1H, dd, *J* = 11.1, 5.4 Hz, H-12), 5.07 (1H, brt, *J* = 7.3 Hz, H-17), 5.23 (2H, brt, *J* = 7.4 Hz, H-2''), 5.81 (1H, s, H-6), 6.43 (1H, d, *J* = 2.3 Hz, H-2'), 6.53 (1H, d, *J* = 2.3 Hz, H-6'); <sup>13</sup>C NMR (CD<sub>3</sub>OD, 151 MHz)  $\delta$  18.0 (CH<sub>3</sub>-4''), 18.2 (CH<sub>3</sub>-19), 25.2 (CH<sub>3</sub>-15), 26.0 (CH<sub>3</sub>-5''), 26.1 (CH<sub>3</sub>-20), 26.3 (CH<sub>3</sub>-14), 27.8 (CH<sub>2</sub>-3), 28.7 (CH<sub>2</sub>-11), 29.2 (CH<sub>2</sub>-1''), 31.1 (CH<sub>2</sub>-16), 34.9 (CH<sub>2</sub>-4), 49.4 (CH-2), 60.8 (4'-OCH<sub>3</sub>), 64.4 (C-10), 64.7 (C-8), 71.1 (C-13), 92.2 (CH-12), 104.7 (CH-6), 115.9 (CH-6'), 121.1 (CH-17), 121.3 (CH-2'), 123.8 (CH-2''), 133.6 (C-3''), 134.5 (C-18), 136.7 (C-3'), 138.1 (C-1'), 146.1 (C-4'), 151.4 (C-5'), 182.1 (C-7), 200.7 (C-5), 208.0 (C-9). Supplementary Figures S5.2.24-S5.2.29.



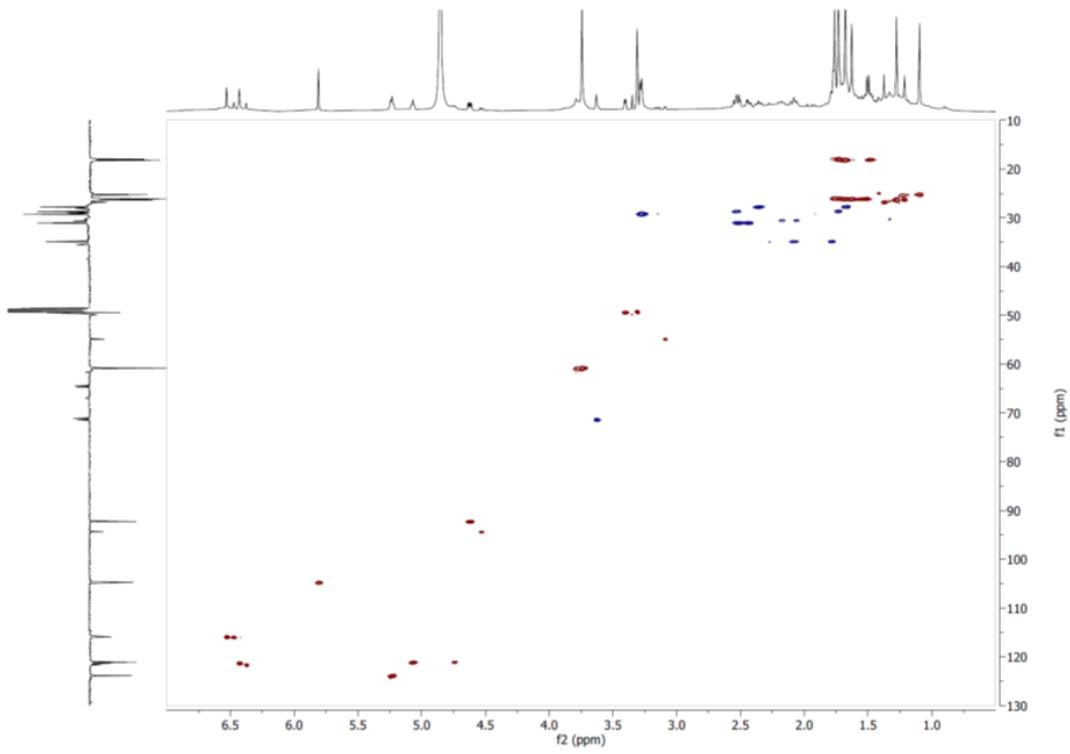
Supplementary Figure S5.2.24.  $^1\text{H}$  NMR spectrum of compound 4 in  $\text{CD}_3\text{OD}$  at 600 MHz



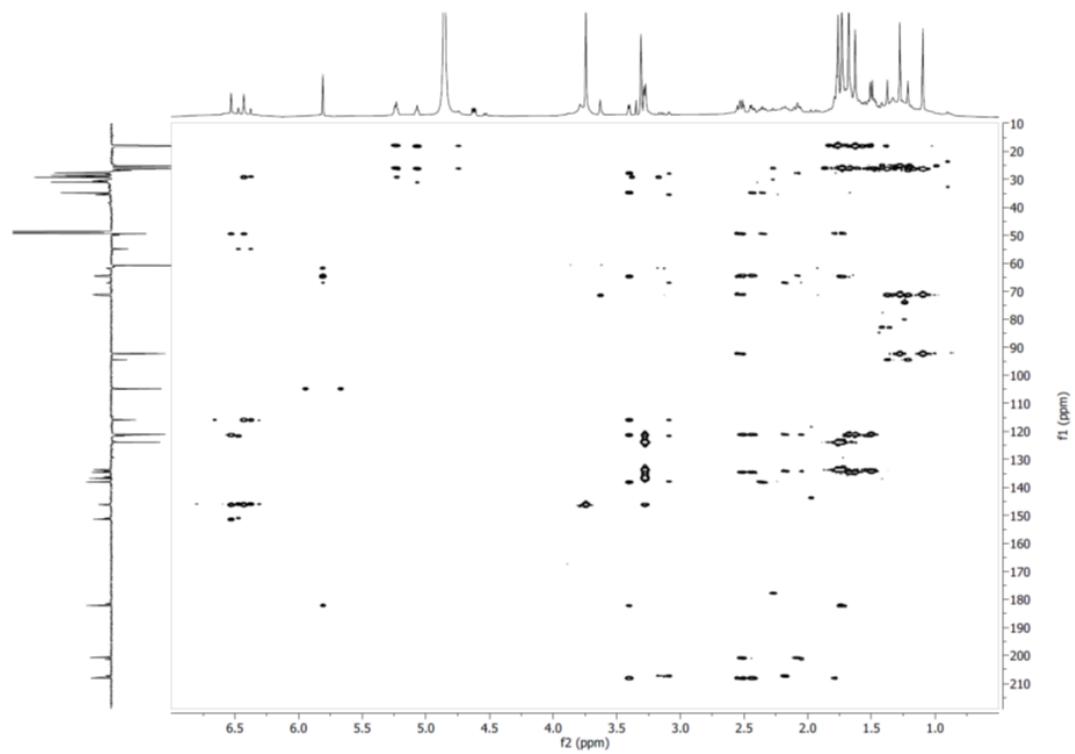
Supplementary Figure S5.2.25. COSY NMR spectrum of compound 4 in  $\text{CD}_3\text{OD}$



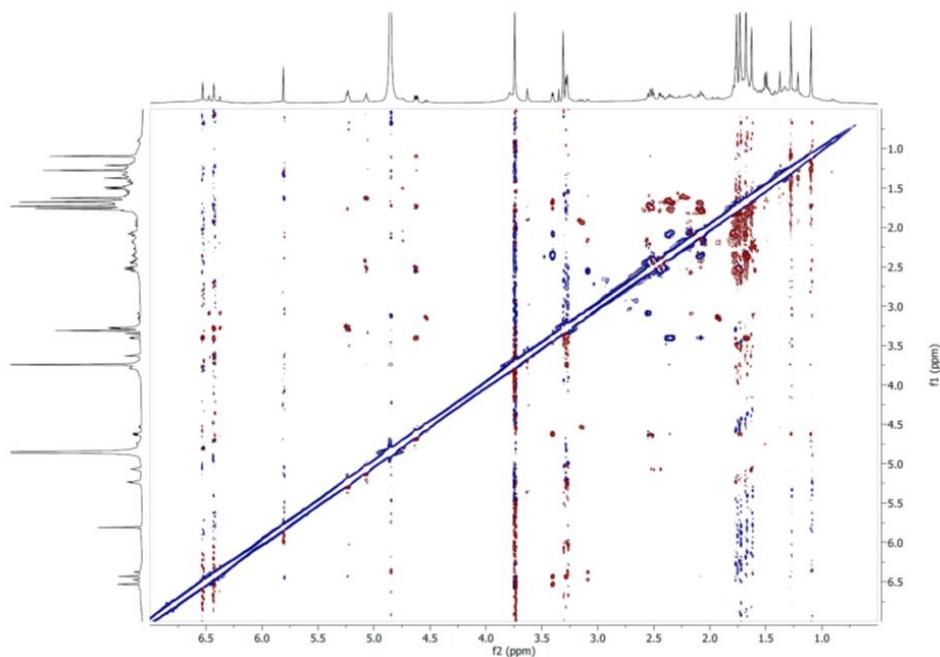
Supplementary Figure S5.2.26.  $^{13}\text{C}$ -DEPTQ NMR spectrum of compound 4 in  $\text{CD}_3\text{OD}$  at 151 MHz



Supplementary Figure S5.2.27. Edited HSQC NMR spectrum of compound 4 in  $\text{CD}_3\text{OD}$

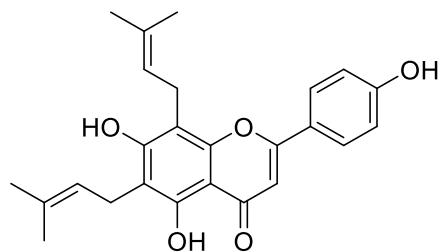


Supplementary Figure S5.2.28. HMBC NMR spectrum of compound 4 in  $\text{CD}_3\text{OD}$



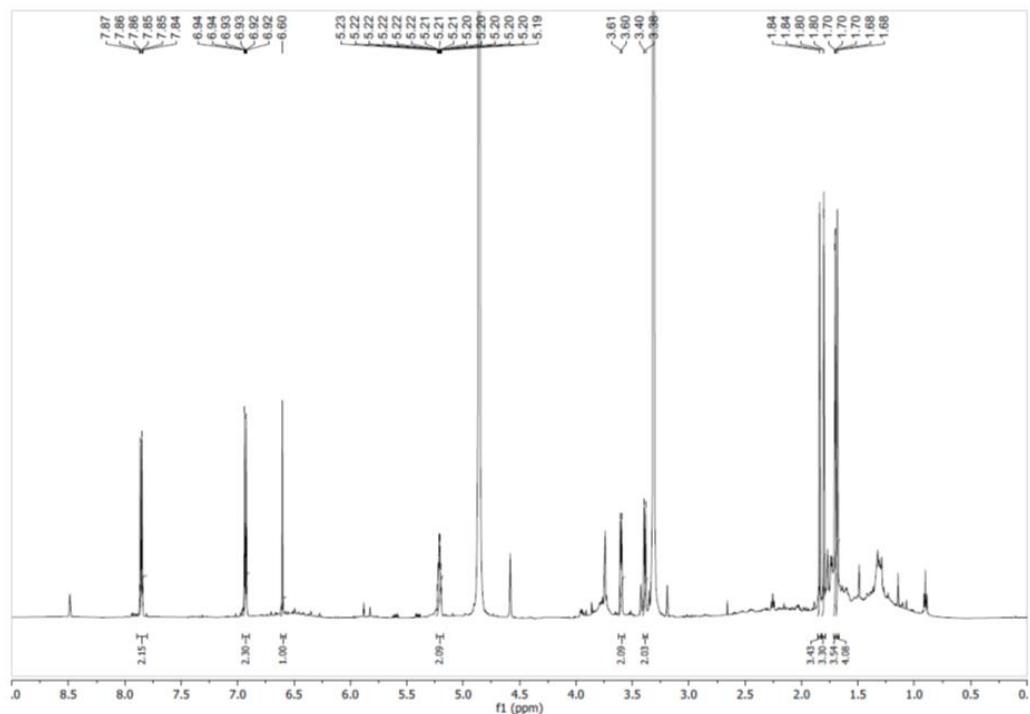
Supplementary Figure S5.2.29. ROESY NMR spectrum of compound 4 in  $\text{CD}_3\text{OD}$

Compound 5: 6,8-diprenylapigenin [25]. Amorphous white powder, HRESIMS  $m/z$  407.1853 [ $M+H$ ]<sup>+</sup> (calculated for C<sub>25</sub>H<sub>27</sub>O<sub>5</sub>, error 0.14 ppm);  $[\alpha]_D^{20}$  -15 (c 0.001, MeOH); UV (c 0.001, MeOH)  $\lambda_{max}$  207, 281, 337 nm.

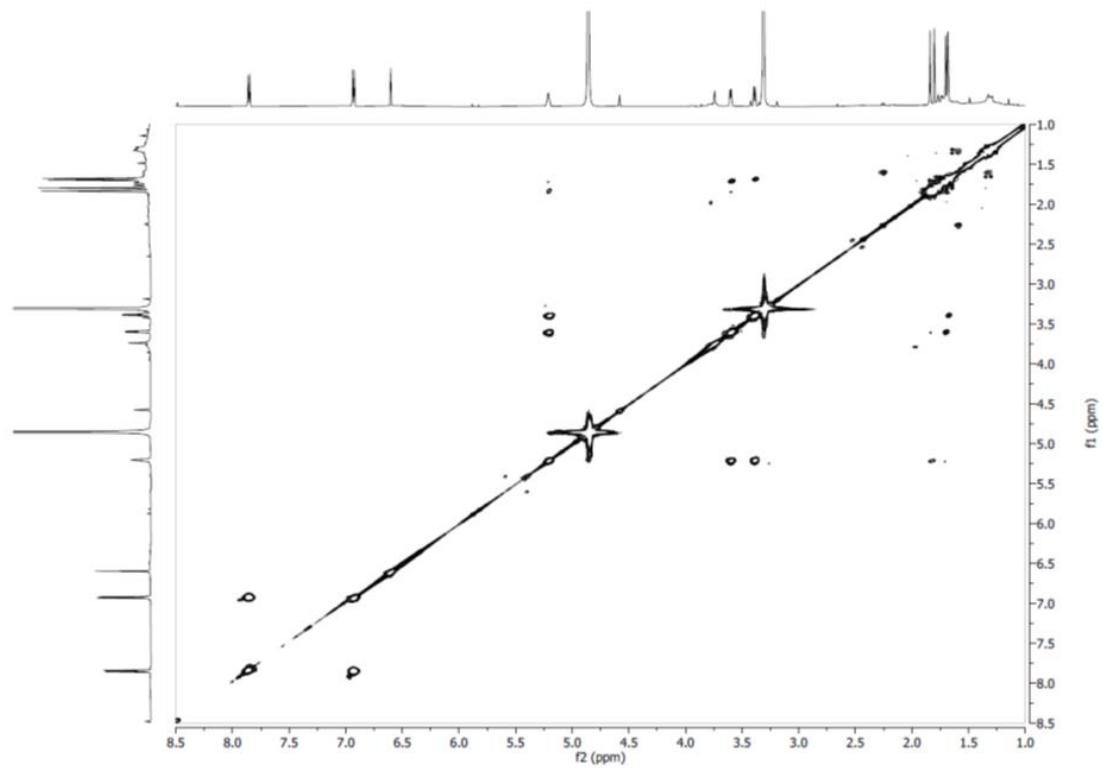


Chemical Formula: C<sub>25</sub>H<sub>26</sub>O<sub>5</sub>  
Exact Mass: 406.18

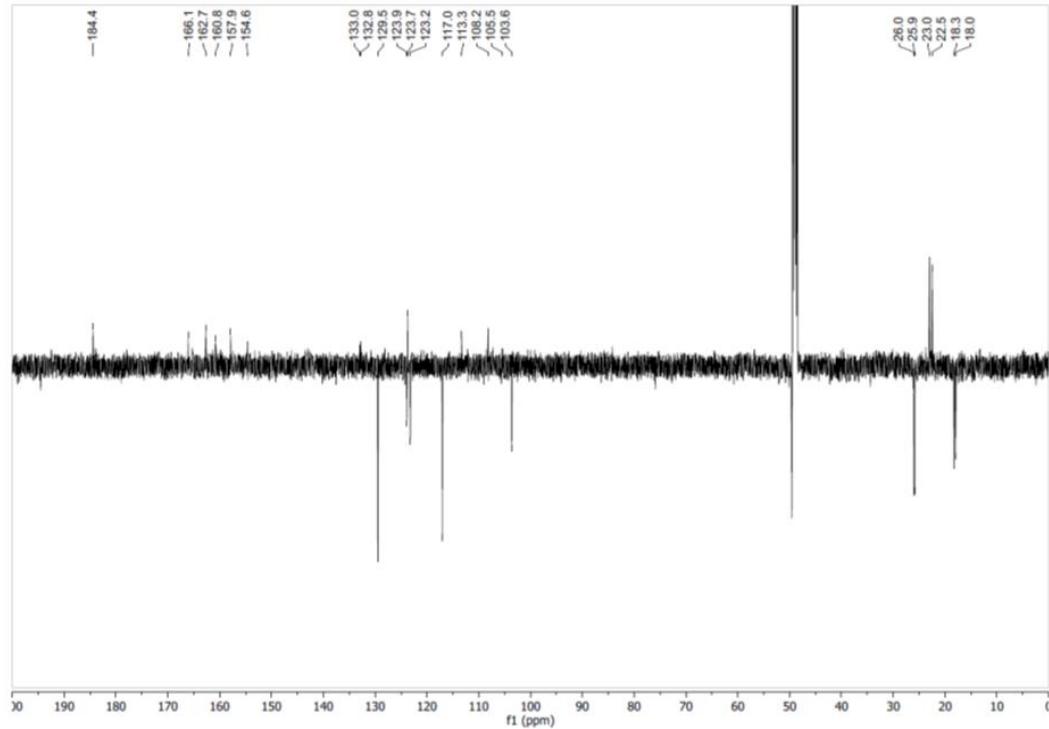
<sup>1</sup>H NMR (CD<sub>3</sub>OD, 600 MHz)  $\delta$  1.68 (3H, d,  $J$  = 1.4 Hz, H<sub>3</sub>-5<sup>'''</sup>), 1.70 (3H, d,  $J$  = 1.5 Hz, H<sub>3</sub>-5<sup>'''</sup>), 1.80 (3H, d,  $J$  = 1.4 Hz, H<sub>3</sub>-4<sup>''</sup>), 1.84 (3H, d,  $J$  = 1.5 Hz, H<sub>3</sub>-4<sup>'''</sup>), 3.39 (2H, d,  $J$  = 7.2 Hz, H<sub>2</sub>-1<sup>''</sup>), 3.60 (2H, d,  $J$  = 6.6 Hz, H<sub>2</sub>-1<sup>'''</sup>), 5.21 (2H, m, H-2<sup>''</sup>, H-2<sup>'''</sup>), 6.60 (1H, s, H-3), 6.93 (2H, d,  $J$  = 8.8 Hz, H-3', H-5'), 7.85 (2H, d,  $J$  = 8.8 Hz, H-2', H-6'); <sup>13</sup>C NMR (CD<sub>3</sub>OD, 151 MHz)  $\delta$  18.0 (CH<sub>3</sub>-4<sup>''</sup>), 18.3 (CH<sub>3</sub>-4<sup>'''</sup>), 22.5 (CH<sub>2</sub>-1<sup>''</sup>), 23.0 (CH<sub>2</sub>-1<sup>'''</sup>), 25.9 (CH<sub>3</sub>-5<sup>'''</sup>), 26.0 (CH<sub>3</sub>-5<sup>''</sup>), 103.6 (CH-3), 105.5 (C-10), 108.2 (C-8), 113.3 (C-6), 117.0 (CH-3', CH-5'), 123.2 (CH-2<sup>''</sup>), 123.7 (C-1'), 123.9 (CH-2<sup>'''</sup>), 129.5 (CH-2', CH-6'), 132.8 (C-3<sup>'''</sup>), 133.0 (C-3<sup>'''</sup>), 154.6 (C-9), 157.9 (C-5), 160.8 (C-7), 162.7 (C-4'), 166.1 (C-2), 184.4 (C-4). Supplementary Figures S5.2.30-S5.2.35.



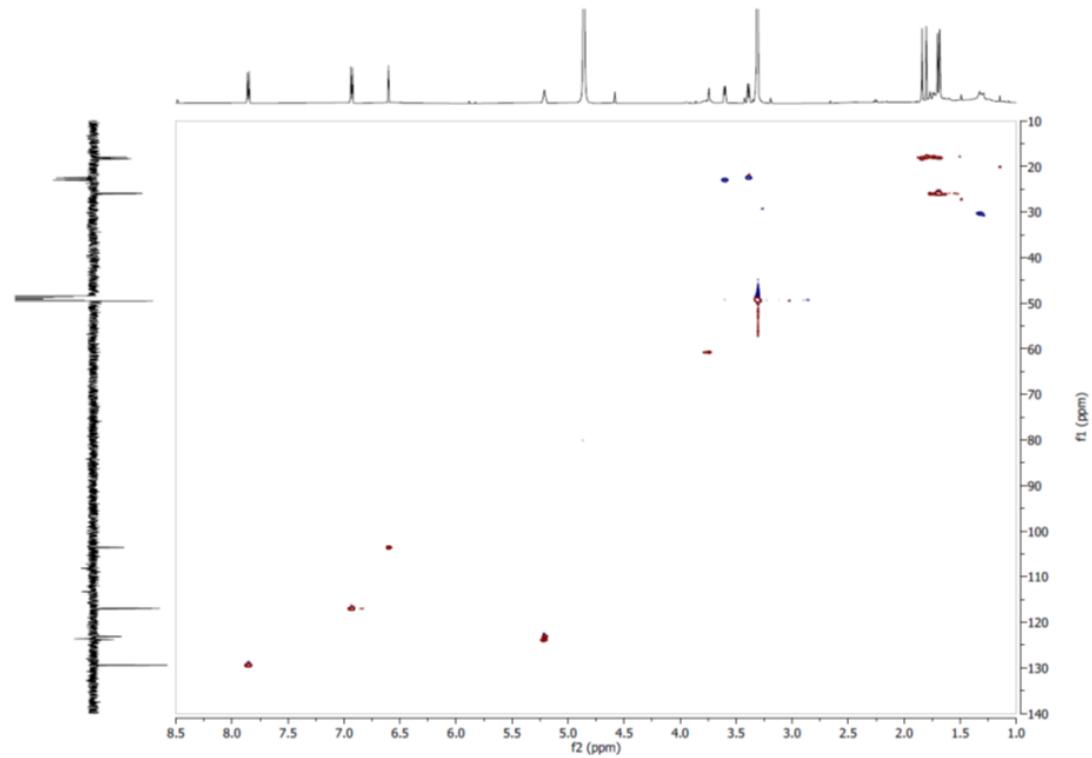
Supplementary Figure S5.2.30.  $^1\text{H}$  NMR spectrum of compound 5 in  $\text{CD}_3\text{OD}$  at 600 MHz



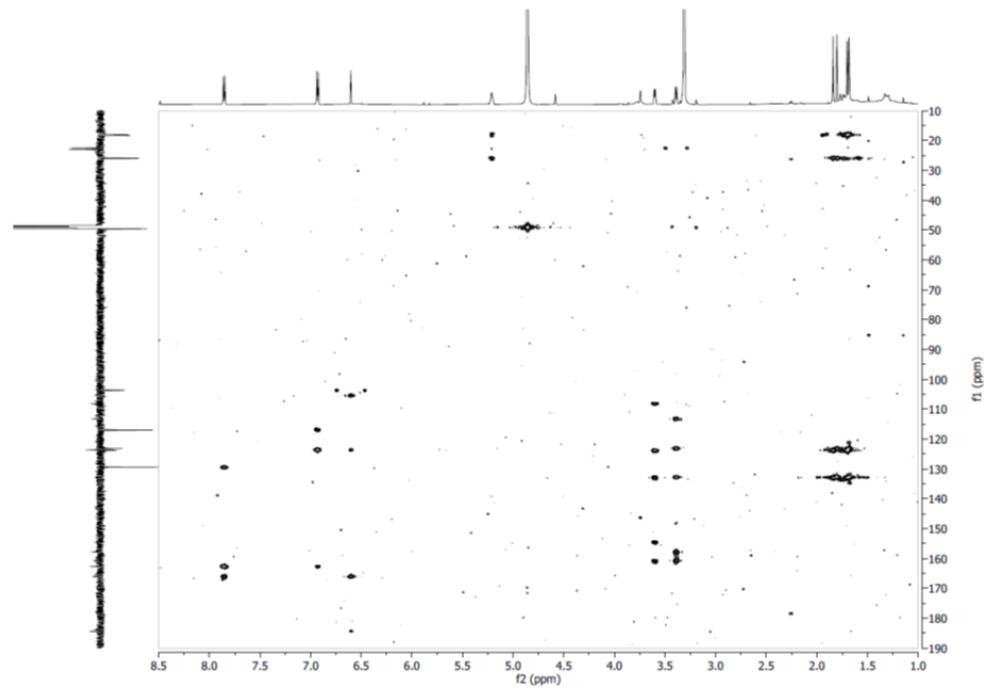
Supplementary Figure S5.2.31. COSY NMR spectrum of compound 5 in  $\text{CD}_3\text{OD}$



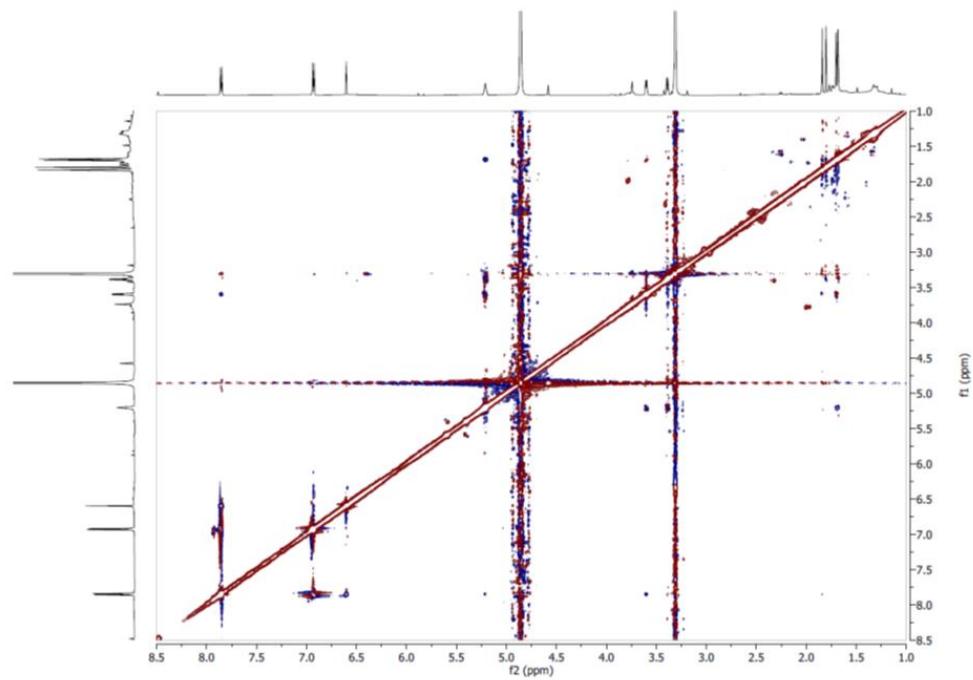
Supplementary Figure S5.2.32.  $^{13}\text{C}$ -DEPTQ NMR spectrum of compound 5 in  $\text{CD}_3\text{OD}$  at 151 MHz



Supplementary Figure S5.2.33. Edited HSQC NMR spectrum of compound 5 in  $\text{CD}_3\text{OD}$

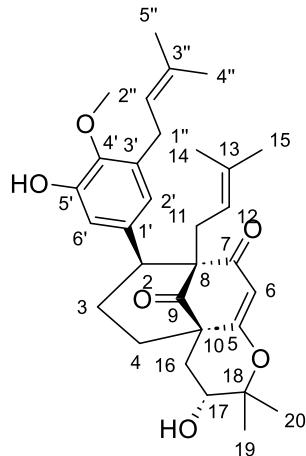


Supplementary Figure S5.2.34. HMBC NMR spectrum of compound 5 in  $\text{CD}_3\text{OD}$



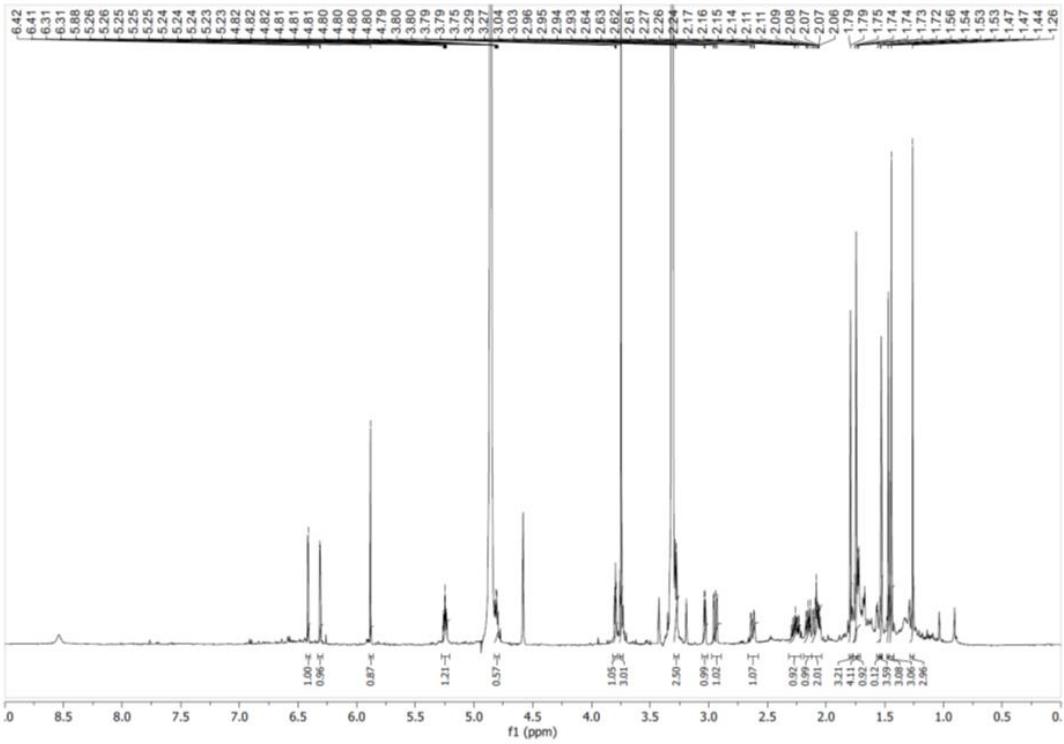
Supplementary Figure S5.2.35. ROESY NMR spectrum of compound 5 in  $\text{CD}_3\text{OD}$

Compound **6** (Hymenotamayonin I): (*2S,8R,10R,17R*)-17-hydroxy-2-(5-hydroxy, 4-methoxy-3-(3-methylbut-2-en-1-yl)phenyl)-18,18-dimethyl-8-(3-methylbut-2-en-1-yl)-5-oxotricyclo[7.3.1.0<sup>5,10</sup>]dodec-5-ene-7,9-dione. Amorphous pale yellow powder, HRESIMS *m/z* 509.2894 [M+H]<sup>+</sup> (calculated for C<sub>31</sub>H<sub>41</sub>O<sub>6</sub>, error -0.65 ppm);  $[\alpha]_D^{20} +18$  (c 0.0005, MeOH); UV (c 0.0005, MeOH)  $\lambda_{\text{max}}$  207, 273 nm.

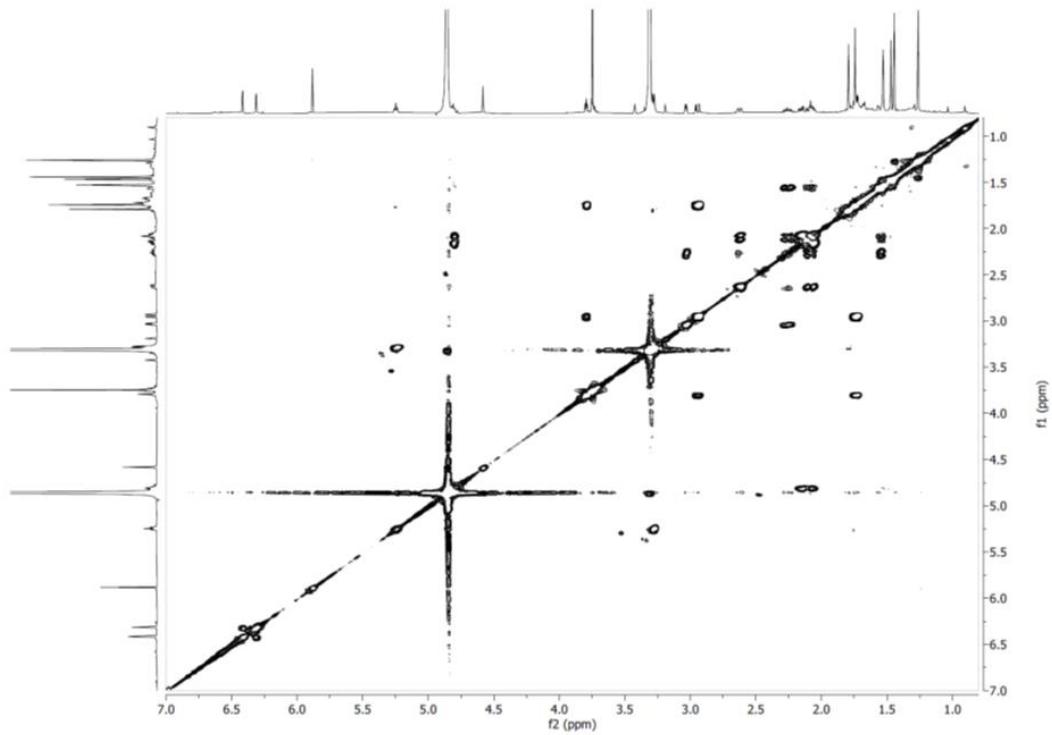


Chemical Formula: C<sub>31</sub>H<sub>40</sub>O<sub>6</sub>  
Exact Mass: 508.28

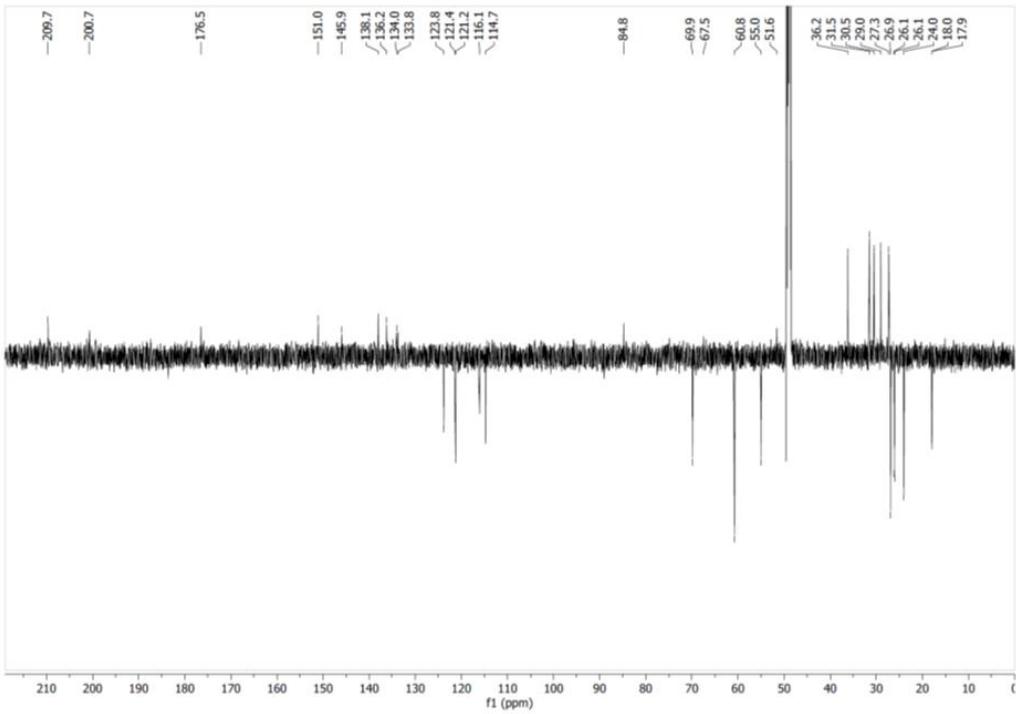
<sup>1</sup>H NMR (CD<sub>3</sub>OD, 600 MHz)  $\delta$  1.26 (3H, s, H<sub>3</sub>-20), 1.44 (3H, s, H<sub>3</sub>-19), 1.47 (3H, d, *J* = 1.4 Hz, H<sub>3</sub>-14), 1.53 (3H, d, *J* = 1.4 Hz, H<sub>3</sub>-15), 1.55 (1H, brd, *J* = 10.8 Hz, H-3eq), 1.74 (1H, dd, *J* = 14.9, 5.3 Hz, H-16b), 1.74 (3H, d, *J* = 1.3 Hz, H<sub>3</sub>-4''), 1.79 (3H, d, *J* = 1.3 Hz, H<sub>3</sub>-5''), 2.09 (1H, td, *J* = 14.5, 4.6 Hz, H-4ax), 2.07 (1H, overlapped, H-11b), 2.15 (1H, dd, *J* = 14.7, 7.8 Hz, H-11a), 2.26 (1H, tt, *J* = 14.2, 5.6 Hz, H-3ax), 2.63 (1H, dd, *J* = 14.5, 4.9 Hz, H-4eq), 2.94 (1H, dd, *J* = 14.9, 3.9 Hz, H-16a), 3.03 (1H, d, *J* = 6.2 Hz, H-2eq), 3.28 (2H, d, *J* = 7.5 Hz, H<sub>2</sub>-1''), 3.75 (3H, s, 4'-OCH<sub>3</sub>), 3.79 (1H, t, *J* = 5.3, 3.9 Hz, H-17), 4.81 (1H, thept, *J* = 7.8, 1.4 Hz, H-12), 5.25 (1H, thept, *J* = 7.5, 1.3 Hz, H-2''), 5.88 (1H, s, H-6), 6.31 (1H, d, *J* = 2.3 Hz, H-2'), 6.42 (1H, d, *J* = 2.3 Hz, H-6'); <sup>13</sup>C NMR (CD<sub>3</sub>OD, 151 MHz)  $\delta$  17.9 (CH<sub>3</sub>-4''), 18.0 (CH<sub>3</sub>-14), 24.0 (CH<sub>3</sub>-19), 26.1 (CH<sub>3</sub>-5''), 26.1 (CH<sub>3</sub>-15), 26.9 (CH<sub>3</sub>-20), 27.3 (CH<sub>2</sub>-3), 29.0 (CH<sub>2</sub>-1''), 30.5 (CH<sub>2</sub>-11), 31.5 (CH<sub>2</sub>-16), 36.2 (CH<sub>2</sub>-4), 51.6 (C-10), 55.0 (CH-2), 60.8 (4'-OCH<sub>3</sub>), 67.5 (C-8), 69.9 (CH-17), 84.8 (C-18), 114.7 (CH-6), 116.1 (CH-6'), 121.2 (CH-12), 121.4 (CH-2'), 123.8 (CH-2''), 133.8 (C-3''), 134.0 (C-13), 136.2 (C-3'), 138.1 (C-1'), 145.9 (C-4'), 151.0 (C-5'), 176.5 (C-5), 200.7 (C-7), 209.7 (C-9). Supplementary Figures S5.2.36-S5.2.41.



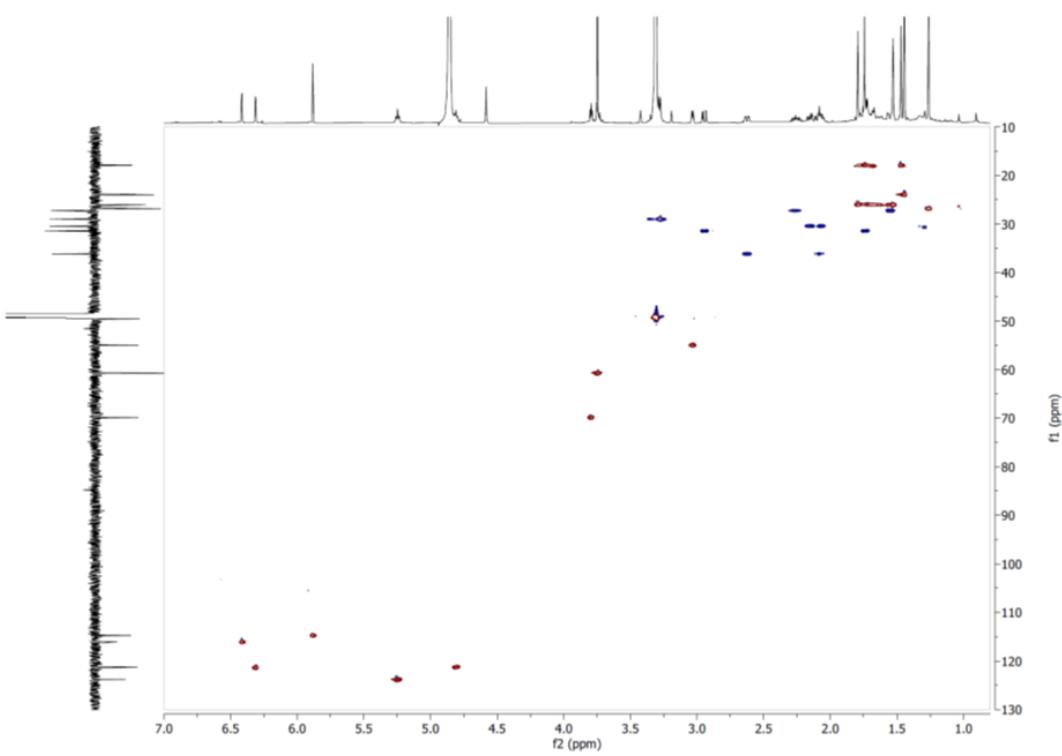
Supplementary Figure S5.2.36.  $^1\text{H}$  NMR spectrum of compound 6 in  $\text{CD}_3\text{OD}$  at 600 MHz



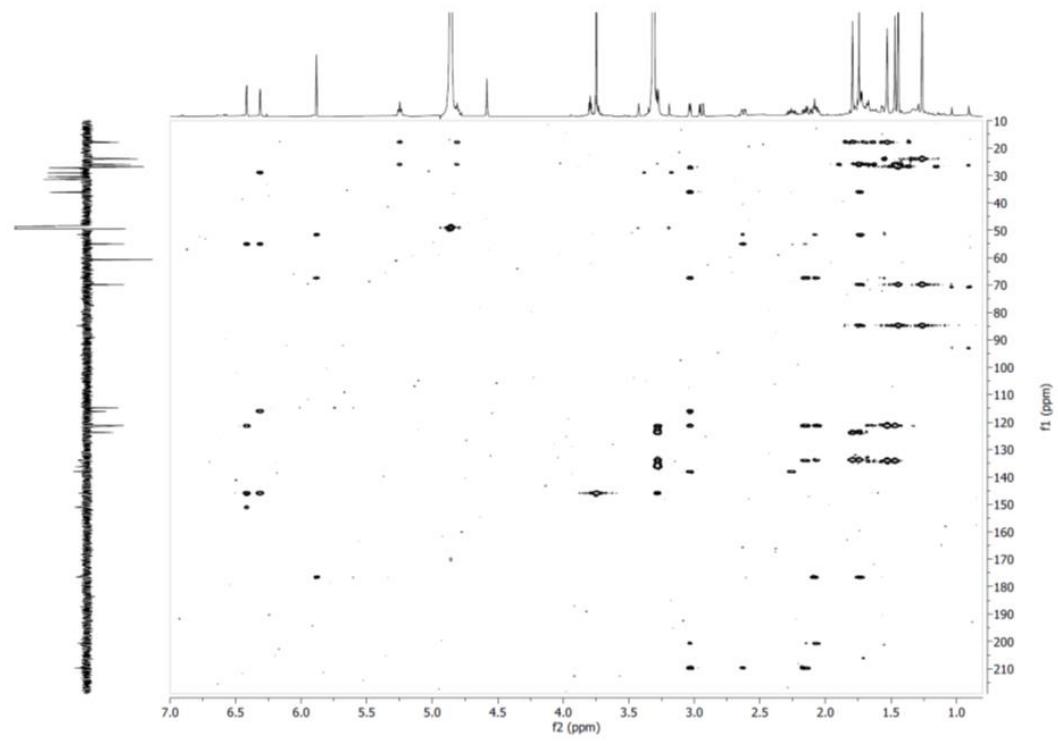
Supplementary Figure S5.2.37. COSY NMR spectrum of compound 6 in  $\text{CD}_3\text{OD}$



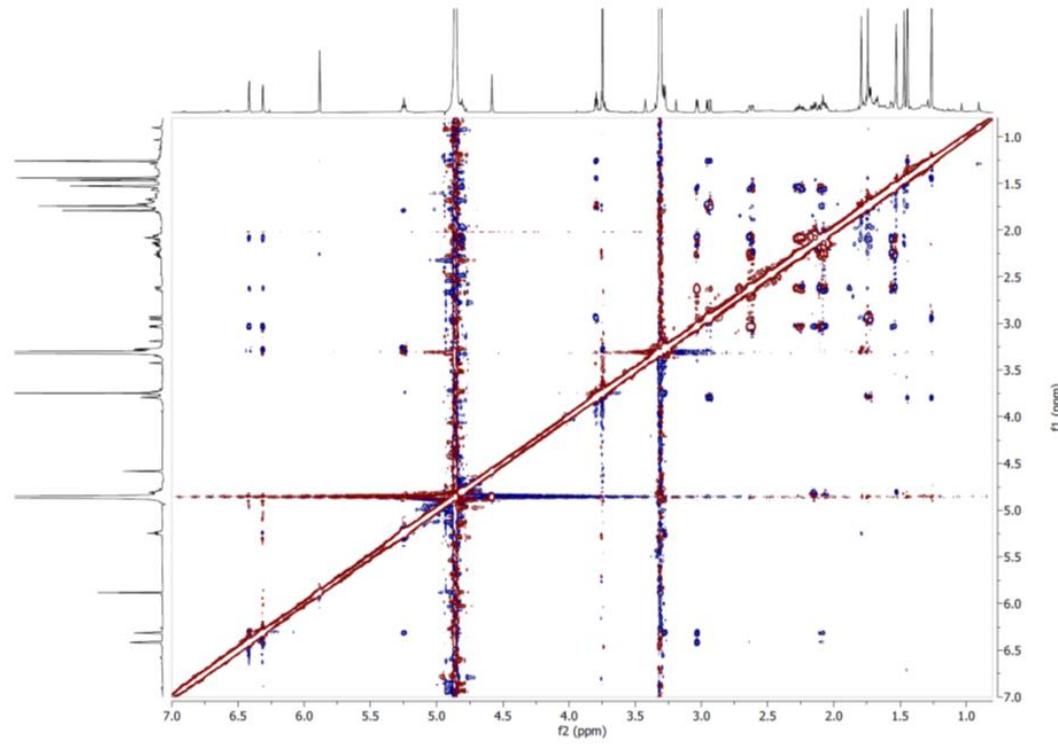
Supplementary Figure S5.2.38.  $^{13}\text{C}$ -DEPTQ NMR spectrum of compound 6 in  $\text{CD}_3\text{OD}$  at 151 MHz



Supplementary Figure S5.2.39. Edited HSQC NMR spectrum of compound 6 in  $\text{CD}_3\text{OD}$

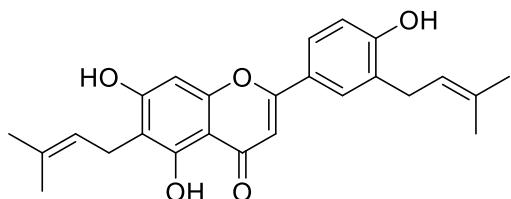


Supplementary Figure S5.2.40. HMBC NMR spectrum of compound 6 in  $\text{CD}_3\text{OD}$



Supplementary Figure S5.2.41. ROESY NMR spectrum of compound 6 in  $\text{CD}_3\text{OD}$

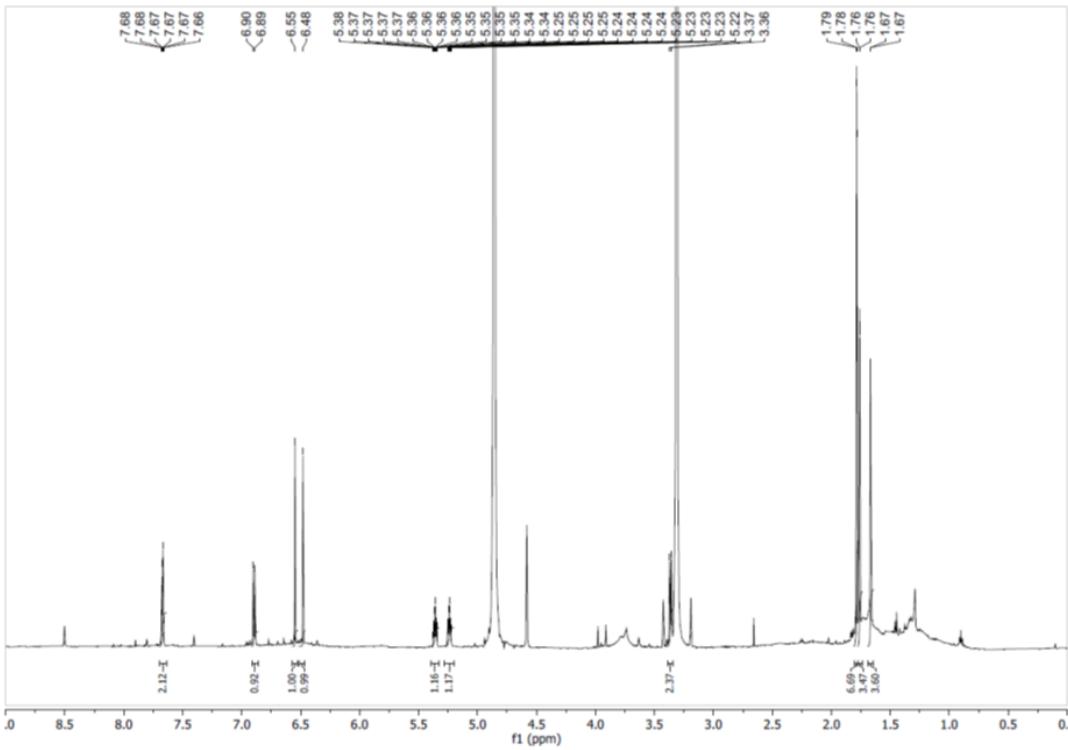
Compound 7: 3',6-diprenyl-diprenylapigenin [26]. Amorphous white powder, HRESIMS  $m/z$  407.1853 [ $M+H$ ]<sup>+</sup> (calculated for C<sub>25</sub>H<sub>27</sub>O<sub>5</sub>, error 0.22 ppm);  $[\alpha]_D^{20}$  -23 (c 0.0004, MeOH); UV (c 0.0004, MeOH)  $\lambda_{\text{max}}$  206, 275, 343 nm.



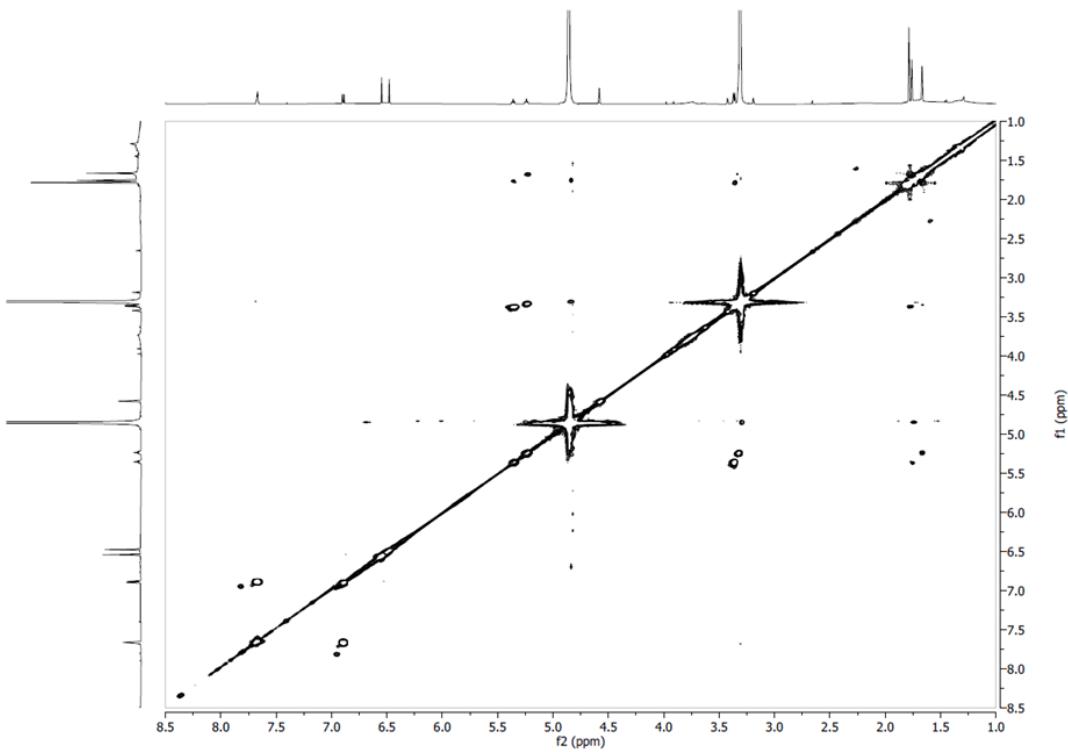
Chemical Formula: C<sub>25</sub>H<sub>26</sub>O<sub>5</sub>  
Exact Mass: 406.18

7. LQ021522

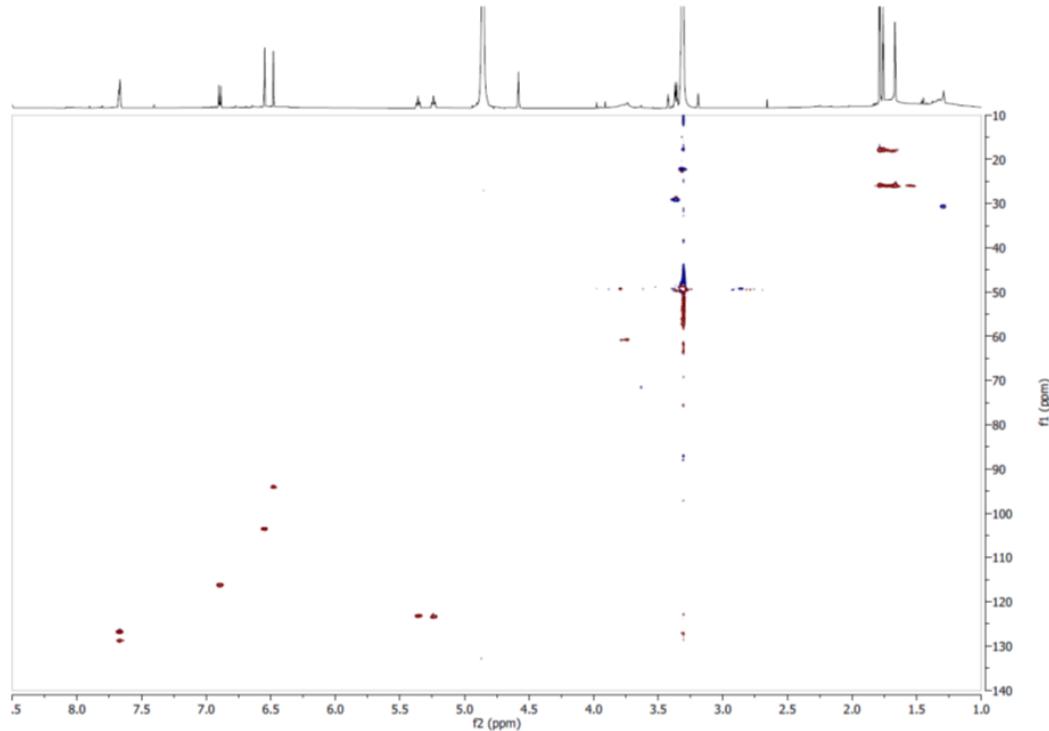
<sup>1</sup>H NMR (CD<sub>3</sub>OD, 600 MHz) δ 1.67 (3H, d,  $J$  = 1.4 Hz, H<sub>3</sub>-5<sup>''</sup>), 1.76 (3H, d,  $J$  = 1.3 Hz, H<sub>3</sub>-10<sup>''</sup>), 1.79 (6H, d,  $J$  = 1.4 Hz, H<sub>3</sub>-4<sup>''</sup>, H<sub>3</sub>-11<sup>''</sup>), 3.32 (2H, overlapped, H<sub>2</sub>-1<sup>''</sup>), 3.36 (2H, d,  $J$  = 7.4 Hz, H<sub>2</sub>-7<sup>''</sup>), 5.24 (1H, thept,  $J$  = 7.0, 1.4 Hz, H-2<sup>''</sup>), 5.36 (1H, thept,  $J$  = 7.4, 1.3 Hz, H-8<sup>''</sup>), 6.48 (1H, s, H-8), 6.55 (1H, s, H-3), 6.89 (1H, d,  $J$  = 9.0 Hz, H-3<sup>''</sup>), 7.67 (2H, m, H-2<sup>''</sup>, H-6<sup>''</sup>); <sup>13</sup>C NMR (CD<sub>3</sub>OD, 151 MHz) δ 17.9 (CH<sub>3</sub>-4<sup>''</sup>, CH<sub>3</sub>-10<sup>''</sup>), 22.3 (CH<sub>2</sub>-1<sup>''</sup>), 25.8 (CH<sub>3</sub>-11<sup>''</sup>), 26.0 (CH<sub>3</sub>-5<sup>''</sup>), 29.2 (CH<sub>2</sub>-7<sup>''</sup>), 94.1 (CH-8), 103.6 (CH-3), 105.1 (C-10), 113.1 (C-6), 116.2 (CH-3<sup>''</sup>), 123.2 (CH-8<sup>''</sup>, C-1<sup>''</sup>), 123.4 (CH-2<sup>''</sup>), 126.8 (CH-2<sup>''</sup>), 128.9 (CH-6<sup>''</sup>), 130.4 (C-5<sup>''</sup>), 132.2 (C-3<sup>''</sup>), 134.0 (C-9<sup>''</sup>), 157.4 (C-9), 159.9 (C-5), 160.5 (C-4<sup>''</sup>), 163.7 (C-7), 166.4 (C-2), 184.1 (C-4). Supplementary Figures S5.2.42-S5.2.46.



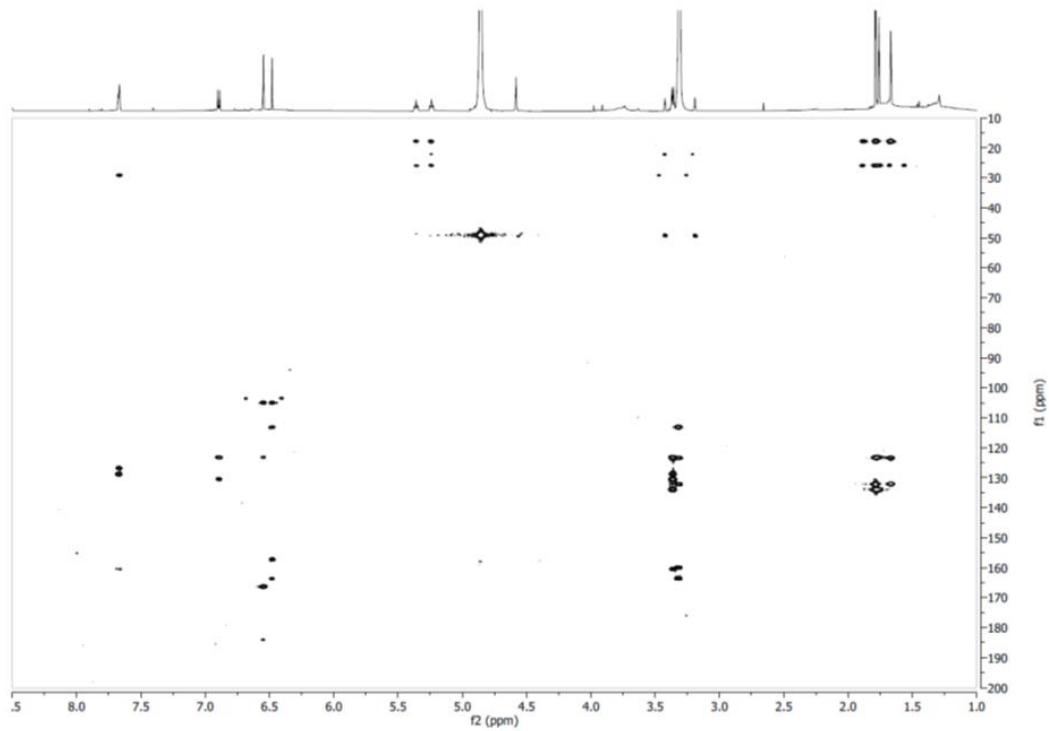
Supplementary Figure S5.2.42.  $^1\text{H}$  NMR spectrum of compound 7 in  $\text{CD}_3\text{OD}$  at 600 MHz.



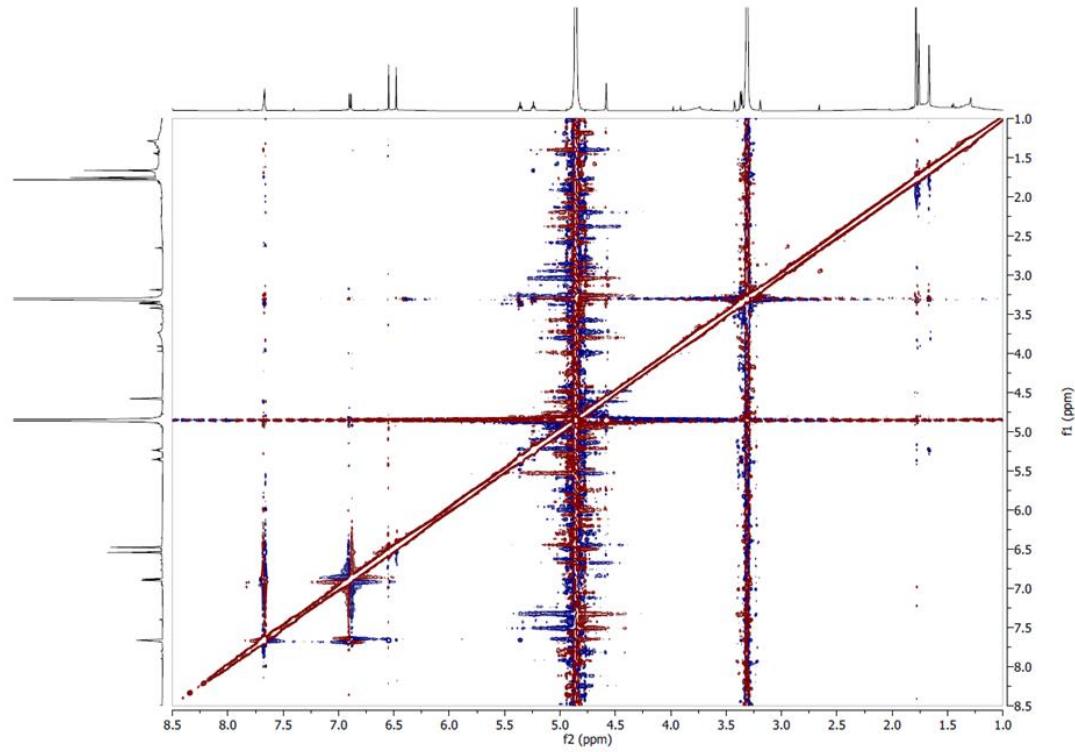
Supplementary Figure S5.2.43. COSY NMR spectrum of compound 7 in  $\text{CD}_3\text{OD}$



Supplementary Figure S5.2.44. Edited HSQC NMR spectrum of compound 7 in  $\text{CD}_3\text{OD}$

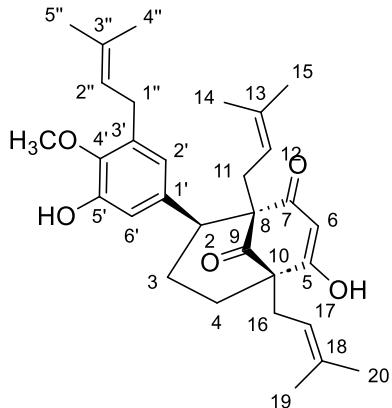


Supplementary Figure S5.2.45. HMBC NMR spectrum of compound 7 in  $\text{CD}_3\text{OD}$



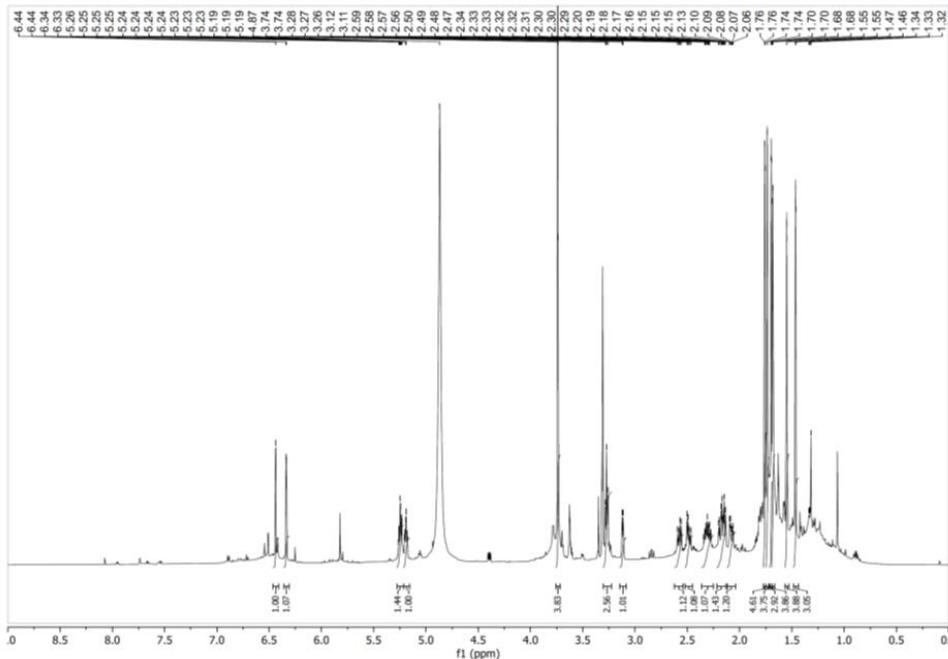
Supplementary Figure S5.2.46. ROESY NMR spectrum of compound 7 in  $\text{CD}_3\text{OD}$

Compound **8** (Hymenotamayonin C): (*2S,8R,10R*)-2-(5-hydroxy-4-methoxy-3-(3-methylbut-2-en-1-yl)phenyl)-5-hydroxy-8,10-bis(3-methylbut-2-en-1-yl)bicyclo[3.3.1]non-6-ene-7,9-dione. Amorphous orange powder, HRESIMS *m/z* 493.2894 [M+H]<sup>+</sup> (calculated for C<sub>31</sub>H<sub>41</sub>O<sub>5</sub>, error -0.34 ppm); [α]<sub>D</sub><sup>20</sup> -14 (c 0.001, MeOH); UV (c 0.001, MeOH) λ<sub>max</sub> 219, 271 nm.

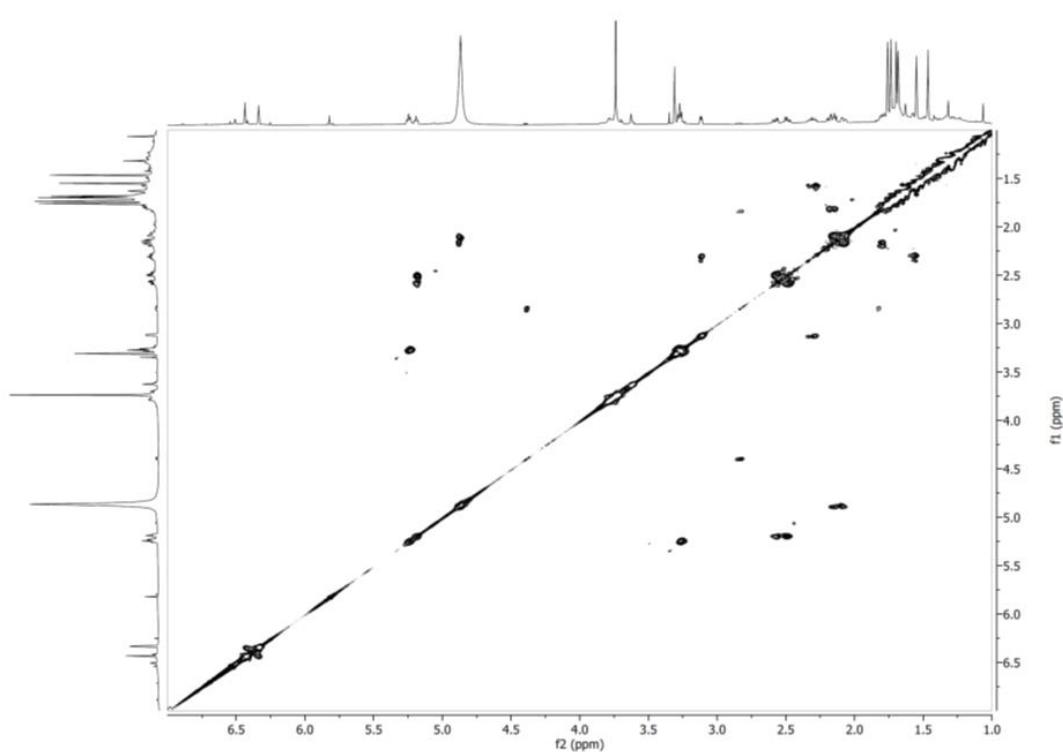


Chemical Formula: C<sub>31</sub>H<sub>40</sub>O<sub>5</sub>  
Exact Mass: 492.29

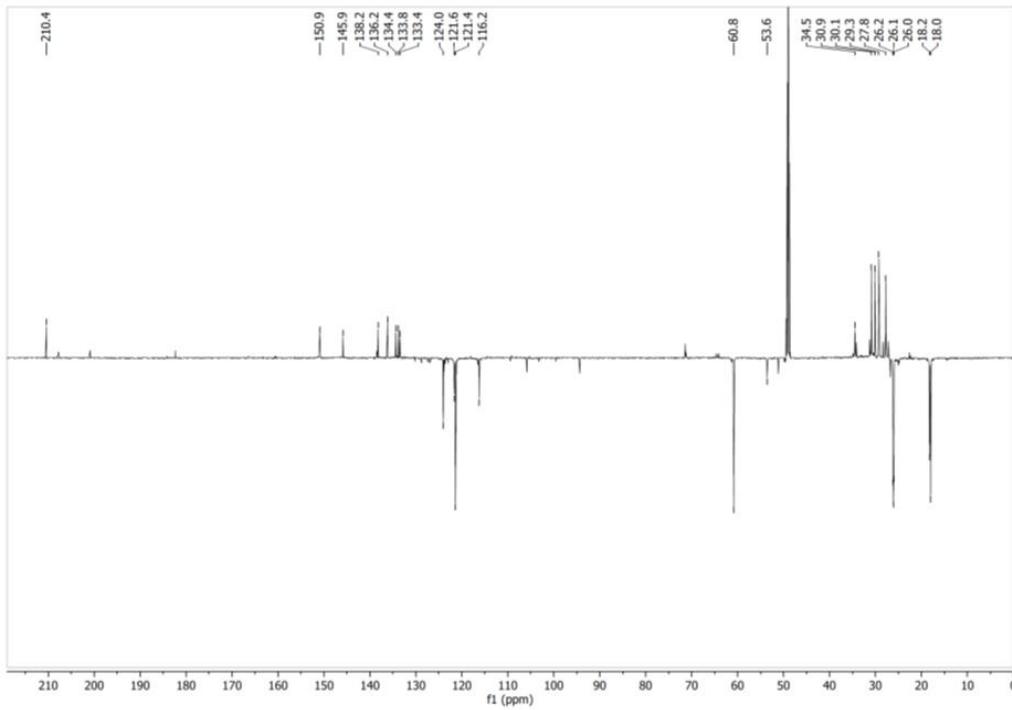
<sup>1</sup>H NMR (CD<sub>3</sub>OD, 600 MHz) δ 1.46 (3H, d, *J* = 1.5 Hz, H<sub>3</sub>-14), 1.55 (3H, d, *J* = 1.5 Hz, H<sub>3</sub>-15), 1.56 (1H, overlapped, H-3eq), 1.68 (3H, d, *J* = 1.4 Hz, H<sub>3</sub>-19), 1.70 (3H, d, *J* = 1.4 Hz, H<sub>3</sub>-20), 1.74 (3H, d, *J* = 1.4 Hz, H<sub>3</sub>-4''), 1.76 (3H, d, *J* = 1.4 Hz, H<sub>3</sub>-5''), 1.79 (1H, overlapped, H-4eq), 2.08 (1H, dd, *J* = 14.2, 5.2 Hz, H-11b), 2.15 (1H, overlapped, H-11a), 2.17 (1H, td, *J* = 13.8, 4.7 Hz, H-4ax), 2.31 (1H, tt, *J* = 13.8, 6.4 Hz, H-3ax), 2.49 (1H, dd, *J* = 14.5, 7.1 Hz, H-16b), 2.58 (1H, dd, *J* = 14.5, 7.1 Hz, H-16a), 3.12 (1H, d, *J* = 6.4 Hz, H-2eq), 3.27 (2H, m, H<sub>2</sub>-1''), 3.74 (3H, s, 4'-OCH<sub>3</sub>), 4.87 (1H, overlapped, H-12), 5.19 (1H, thept, *J* = 7.1, 1.5 Hz, H-17), 5.25 (1H, thept, *J* = 7.5, 1.4 Hz, 2''), 6.34 (1H, d, *J* = 2.3 Hz, H-2'), 6.44 (1H, d, *J* = 2.3 Hz, H-6'); <sup>13</sup>C NMR (CD<sub>3</sub>OD, 151 MHz) δ 18.0 (CH<sub>3</sub>-4''), 18.2 (CH<sub>3</sub>-19), 26.0 (CH<sub>3</sub>-5''), 26.1 (CH<sub>3</sub>-15), 26.2 (CH<sub>3</sub>-20), 27.8 (CH<sub>2</sub>-3), 29.3 (CH<sub>2</sub>-1''), 30.1 (CH<sub>2</sub>-11), 30.9 (CH<sub>2</sub>-16), 34.5 (CH<sub>2</sub>-4), 53.6 (CH-2), 60.8 (4'-OCH<sub>3</sub>), 116.2 (CH-6'), 121.4 (CH-12, CH-17), 121.6 (CH-2'), 124.0 (CH-2''), 133.4 (C-3''), 133.8 (C-13), 134.4 (C-18), 136.2 (C-3'), 138.2 (C-1'), 145.9 (C-4'), 150.9 (C-5'), 210.4 (C-9). **Supplementary Figures S5.2.47-S5.2.52.**



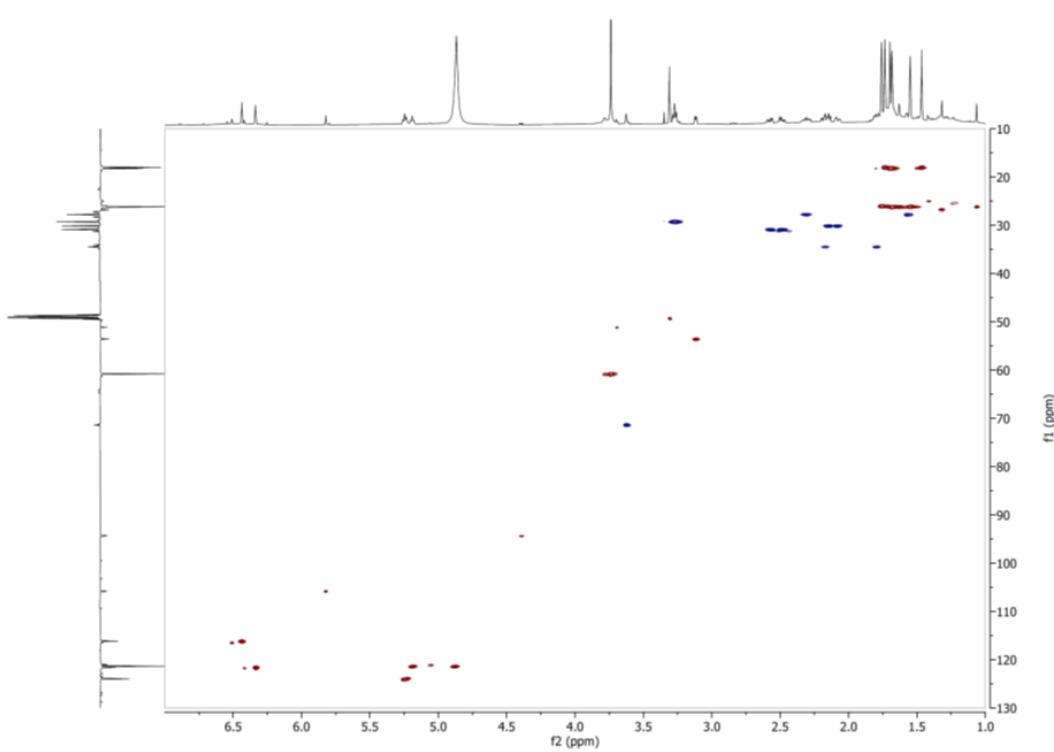
Supplementary Figure S5.2.47.  $^1\text{H}$  NMR spectrum of compound 8 in  $\text{CD}_3\text{OD}$  at 600 MHz



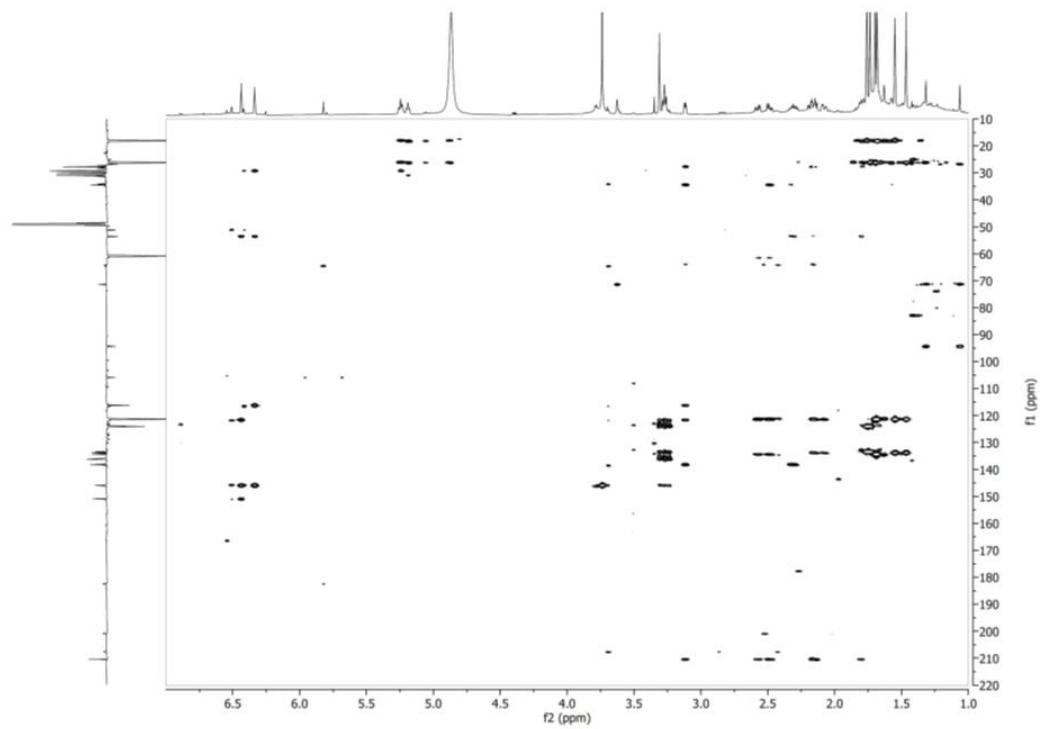
Supplementary Figure S5.2.48. COSY NMR spectrum of compound 8 in  $\text{CD}_3\text{OD}$



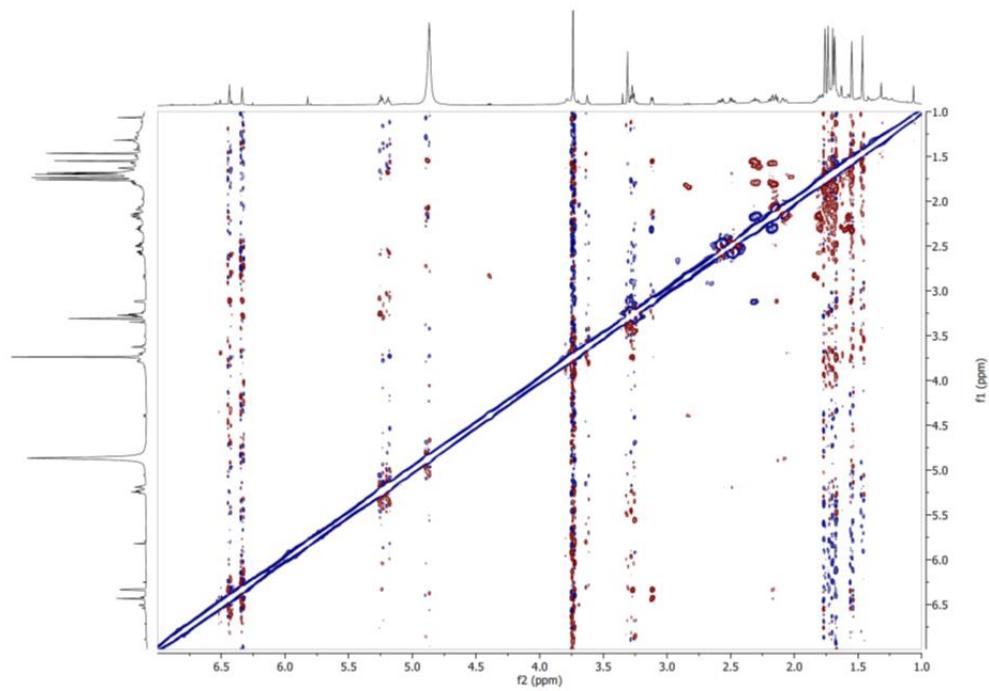
Supplementary Figure S5.2.49.  $^{13}\text{C}$ -DEPTQ NMR spectrum of compound 8 in  $\text{CD}_3\text{OD}$  at 151 MHz



Supplementary Figure S5.2.50. Edited HSQC NMR spectrum of compound 8 in  $\text{CD}_3\text{OD}$

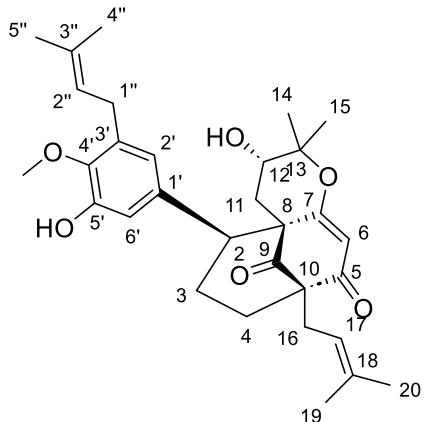


Supplementary Figure S5.2.51. HMBC NMR spectrum of compound 8 in  $\text{CD}_3\text{OD}$



Supplementary Figure S5.2.52. ROESY NMR spectrum of compound 8 in  $\text{CD}_3\text{OD}$

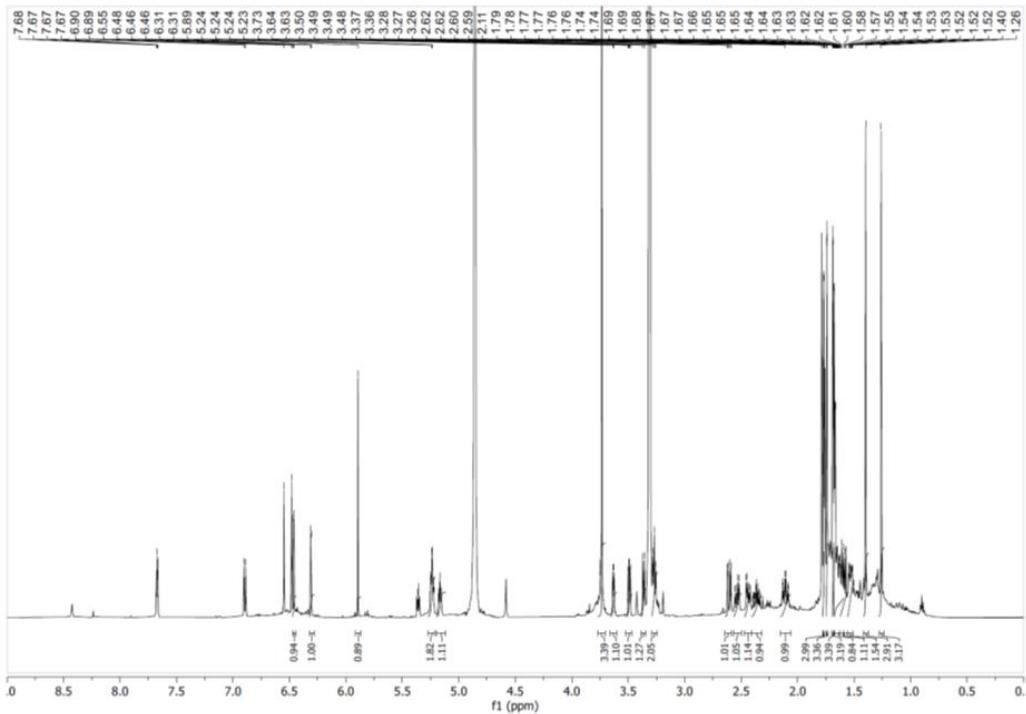
Compound **9** (Hymenotamayonin J): (*2S,8R,10R,12S*)-12-hydroxy-2-(5-hydroxy, 4-methoxy-3-(3-methylbut-2-en-1-yl)phenyl)-13,13-dimethyl-10-(3-methylbut-2-en-1-yl)-7-oxotricyclo[7.3.1.0<sup>7,8</sup>]dodec-5-ene-5,9-dione. . Amorphous orange powder, HRESIMS *m/z* 509.2893 [M+H]<sup>+</sup> (calculated for C<sub>31</sub>H<sub>41</sub>O<sub>6</sub>, error -0.83 ppm);  $[\alpha]_D^{20} -20$  (c 0.002, MeOH); UV (c 0.002, MeOH)  $\lambda_{\text{max}}$  217, 276, 344 nm.



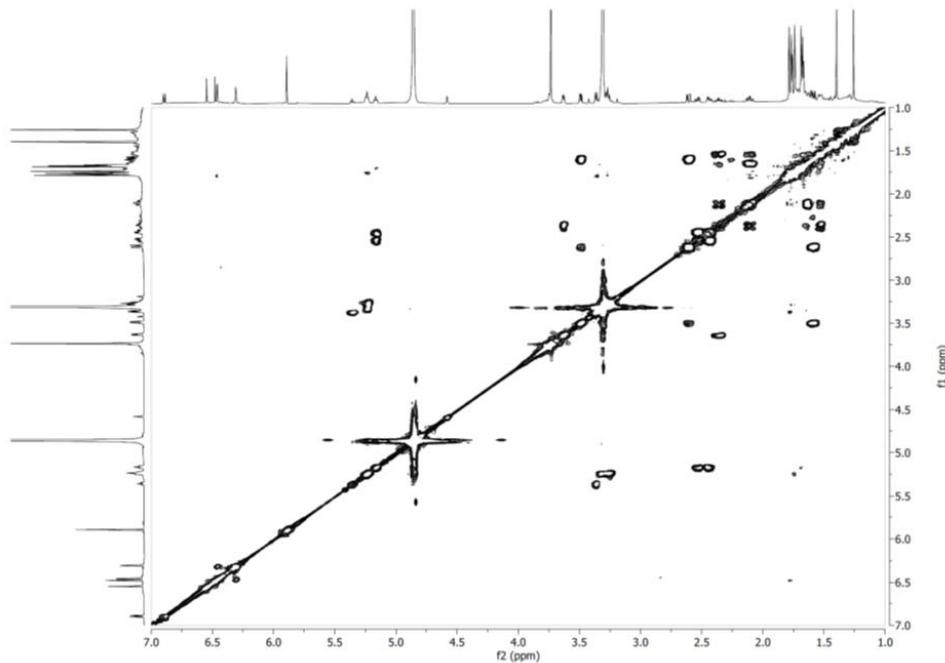
Chemical Formula: C<sub>31</sub>H<sub>40</sub>O<sub>6</sub>

Exact Mass: 508.28

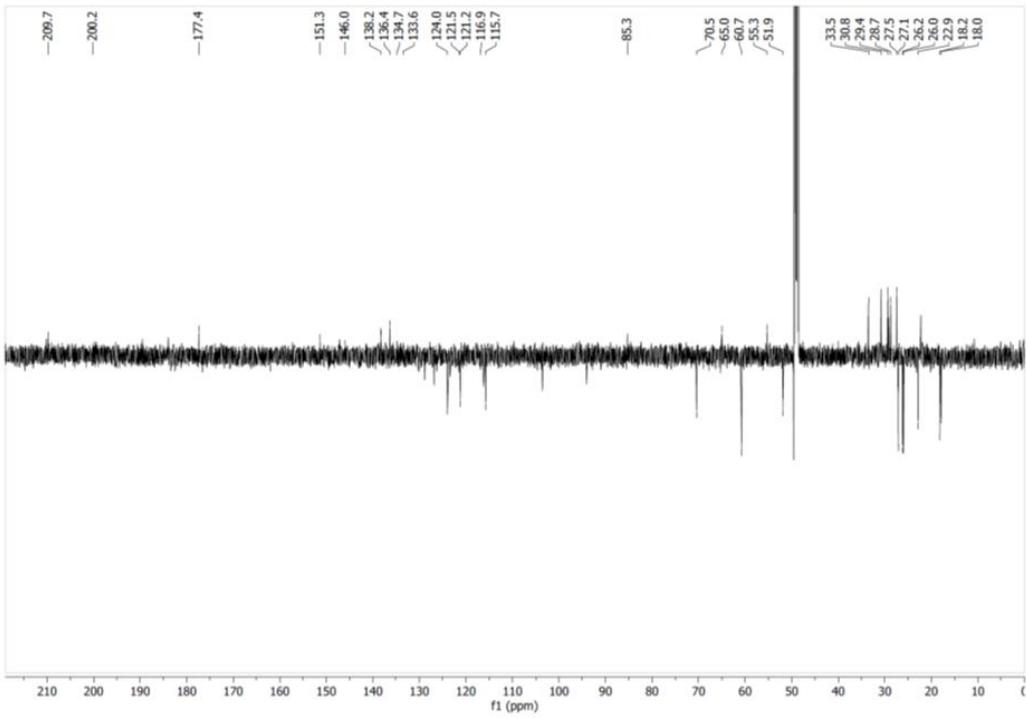
<sup>1</sup>H NMR (CD<sub>3</sub>OD, 600 MHz) δ 1.46 (3H, d, *J* = 1.5 Hz, H<sub>3</sub>-14), 1.55 (3H, d, *J* = 1.5 Hz, H<sub>3</sub>-15), 1.56 (1H, overlapped, H-3eq), 1.68 (3H, d, *J* = 1.4 Hz, H<sub>3</sub>-19), 1.70 (3H, d, *J* = 1.4 Hz, H<sub>3</sub>-20), 1.74 (3H, d, *J* = 1.4 Hz, H<sub>3</sub>-4''), 1.76 (3H, d, *J* = 1.4 Hz, H<sub>3</sub>-5''), 1.79 (1H, overlapped, H-4eq), 2.08 (1H, dd, *J* = 14.2, 5.2 Hz, H-11b), 2.15 (1H, overlapped, H-11a), 2.17 (1H, td, *J* = 13.8, 4.7 Hz, H-4ax), 2.31 (1H, tt, *J* = 13.8, 6.4 Hz, H-3ax), 2.49 (1H, dd, *J* = 14.5, 7.1 Hz, H-16b), 2.58 (1H, dd, *J* = 14.5, 7.1 Hz, H-16a), 3.12 (1H, d, *J* = 6.4 Hz, H-2eq), 3.27 (2H, m, H<sub>2</sub>-1''), 3.74 (3H, s, 4'-OCH<sub>3</sub>), 4.87 (1H, overlapped, H-12), 5.19 (1H, thept, *J* = 7.1, 1.5 Hz, H-17), 5.25 (1H, thept, *J* = 7.5, 1.4 Hz, 2''); <sup>13</sup>C NMR (CD<sub>3</sub>OD, 151 MHz) δ 18.0 (CH<sub>3</sub>-4''), 18.2 (CH<sub>3</sub>-19), 26.0 (CH<sub>3</sub>-5''), 26.1 (CH<sub>3</sub>-15), 26.2 (CH<sub>3</sub>-20), 27.8 (CH<sub>2</sub>-3), 29.3 (CH<sub>2</sub>-1''), 30.1 (CH<sub>2</sub>-11), 30.9 (CH<sub>2</sub>-16), 34.5 (CH<sub>2</sub>-4), 53.6 (CH-2), 60.8 (4'-OCH<sub>3</sub>), 116.2 (CH-6''), 121.4 (CH-12, CH-17), 121.6 (CH-2''), 124.0 (CH-2''), 133.4 (C-3''), 133.8 (C-13), 134.4 (C-18), 136.2 (C-3''), 138.2 (C-1''), 145.9 (C-4''), 150.9 (C-5''), 210.4 (C-9). Supplementary Figures S5.2.53-S5.2.58.



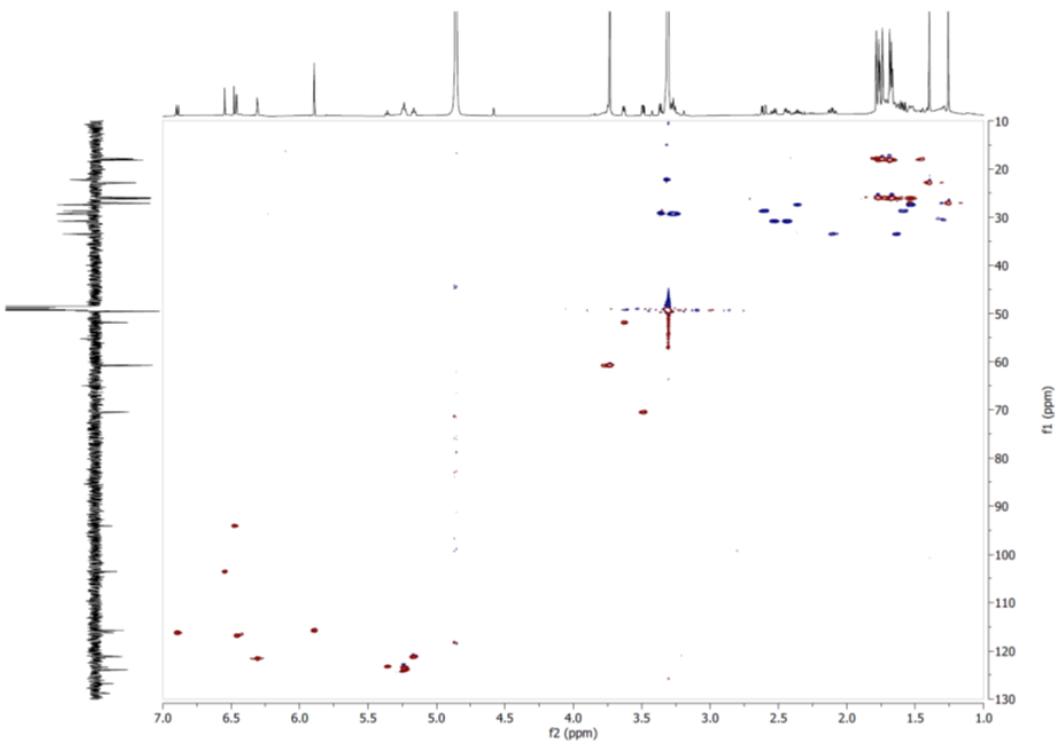
Supplementary Figure S5.2.53.  $^1\text{H}$  NMR spectrum of compound 9 in  $\text{CD}_3\text{OD}$  at 600 MHz



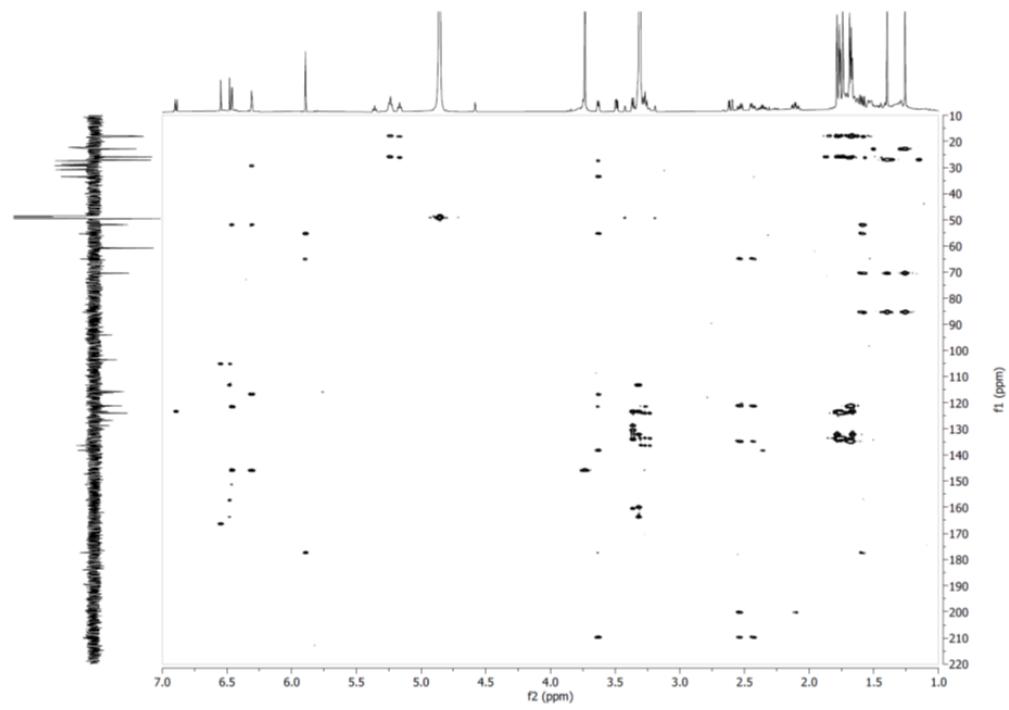
Supplementary Figure S5.2.54. COSY NMR spectrum of compound 9 in CD<sub>3</sub>OD



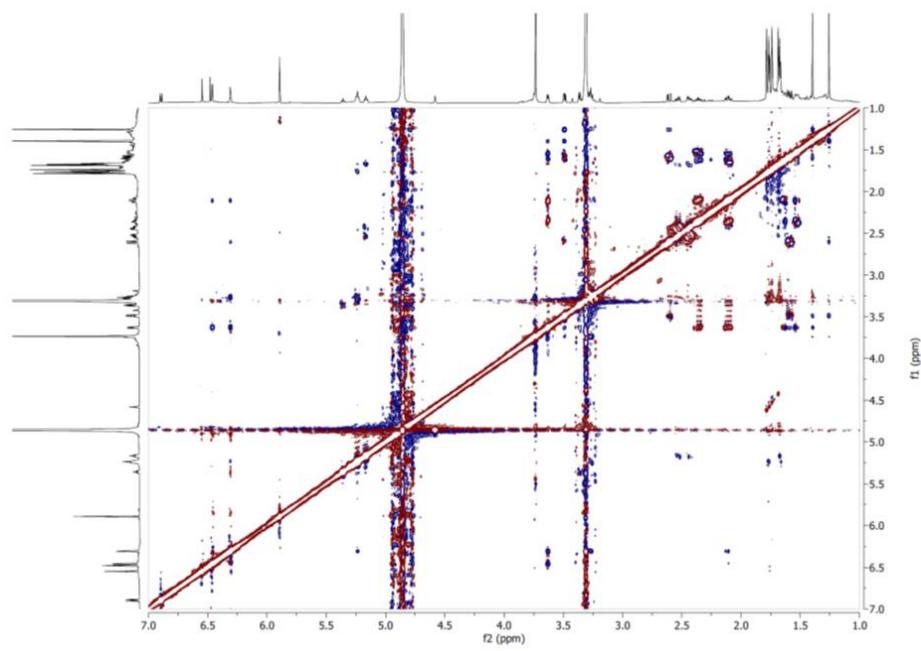
Supplementary Figure S5.2.55.  $^{13}\text{C}$ -DEPTQ NMR spectrum of compound 9 in  $\text{CD}_3\text{OD}$  at 151 MHz



Supplementary Figure S5.2.56. Edited HSQC NMR spectrum of compound 9 in  $\text{CD}_3\text{OD}$

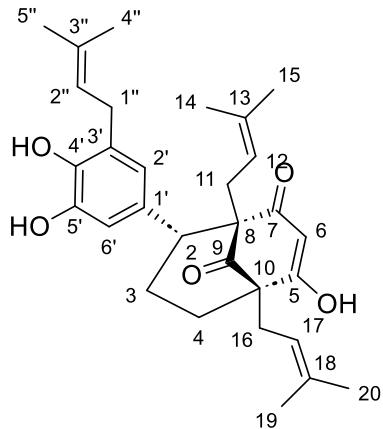


Supplementary Figure S5.2.57. HMBC NMR spectrum of compound 9 in  $\text{CD}_3\text{OD}$



Supplementary Figure S5.2.58. ROESY NMR spectrum of compound 9 in  $\text{CD}_3\text{OD}$

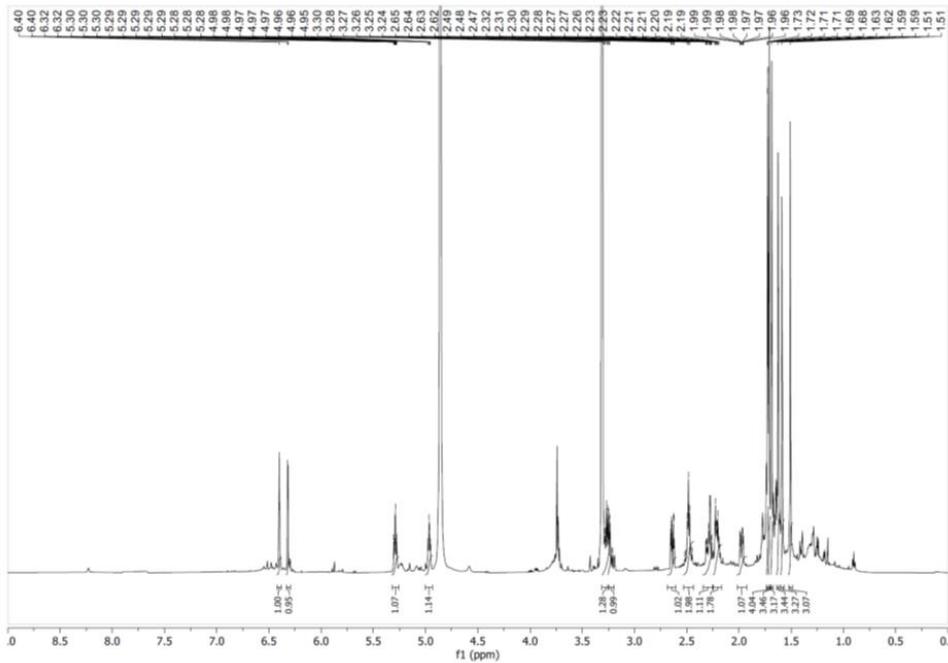
Compound **10** (Hymenotamayonin B): (*2R,8R,10R*)-2-(4,5-dihydroxy-3-(3-methylbut-2-en-1-yl)phenyl)-5-hydroxy-8,10-bis(3-methylbut-2-en-1-yl)bicyclo[3.3.1]non-6-ene-7,9-dione. Amorphous orange powder, HRESIMS *m/z* 479.2791 [M+H]<sup>+</sup> (calculated for C<sub>30</sub>H<sub>39</sub>O<sub>5</sub>, error -0.19 ppm); [α]<sub>D</sub><sup>20</sup> -12 (c 0.002, MeOH); UV (c 0.002, MeOH) λ<sub>max</sub> 221, 273 nm.



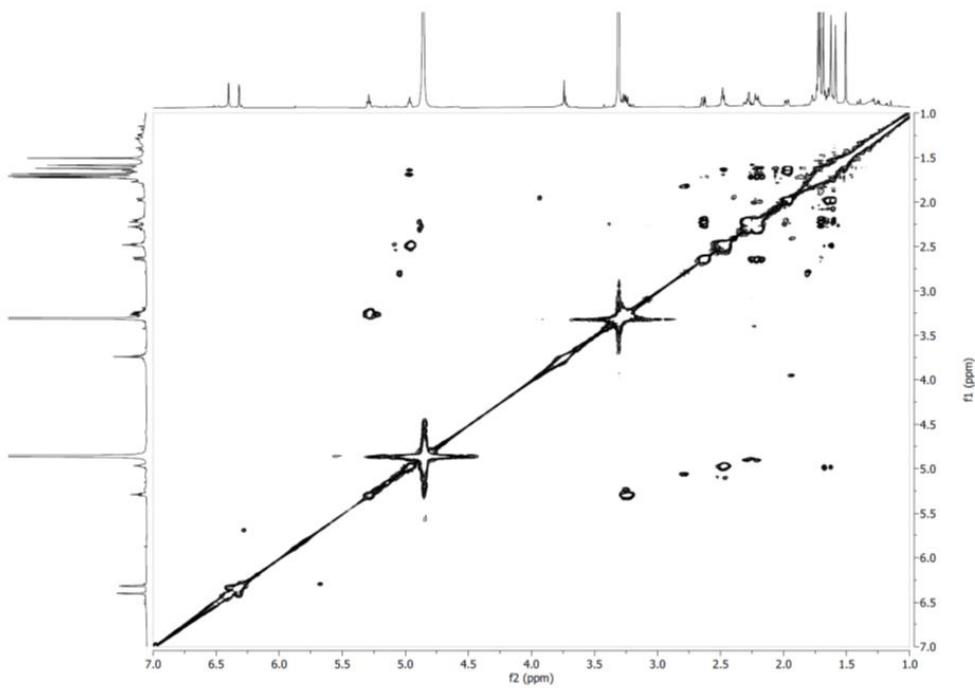
Chemical Formula: C<sub>30</sub>H<sub>38</sub>O<sub>5</sub>  
Exact Mass: 478.27

<sup>1</sup>H NMR (CD<sub>3</sub>OD, 600 MHz) δ 1.51 (3H, d, *J* = 1.5 Hz, H<sub>3</sub>-14), 1.59 (3H, d, *J* = 1.5 Hz, H<sub>3</sub>-15), 1.63 (3H, d, *J* = 1.5 Hz, H<sub>3</sub>-20), 1.64 (1H, overlapped, H-4ax), 1.69 (3H, d, *J* = 1.5 Hz, H<sub>3</sub>-19), 1.71 (3H, d, *J* = 1.4 Hz, H<sub>3</sub>-4''), 1.71 (1H, overlapped, H-3eq), 1.73 (3H, d, *J* = 1.4 Hz, H<sub>3</sub>-5''), 1.97 (1H, ddd, *J* = 13.1, 4.9, 1.8 Hz, H-4eq), 2.21 (2H, m, H-3ax, H-11b), 2.30 (1H, dd, *J* = 15.0, 6.7 Hz, H-11a), 2.48 (2H, m, H<sub>2</sub>-16), 2.64 (1H, dd, *J* = 13.2, 4.0 Hz, H-2ax), 3.23 (1H, dd, *J* = 15.6, 7.4 Hz, H-1''b), 3.28 (1H, dd, *J* = 15.6, 7.4 Hz, H-1''a), 4.87 (1H, overlapped, H-12), 4.97 (1H, thept, *J* = 6.9, 1.5 Hz, H-17), 5.29 (1H, thept, *J* = 7.4, 1.4 Hz, H-2''), 6.32 (1H, d, *J* = 2.2 Hz, H-2'), 6.40 (1H, d, *J* = 2.2 Hz, H-6'); <sup>13</sup>C NMR (CD<sub>3</sub>OD, 151 MHz) δ 17.9 (CH<sub>3</sub>-4''), 18.2 (CH<sub>3</sub>-14, CH<sub>3</sub>-19), 26.0 (CH<sub>3</sub>-5''), 26.1 (CH<sub>3</sub>-15), 26.1 (CH<sub>3</sub>-20), 28.1 (CH<sub>2</sub>-3), 29.2 (CH<sub>2</sub>-1''), 29.8 (CH<sub>2</sub>-11), 30.9 (CH<sub>2</sub>-16), 39.2 (CH<sub>2</sub>-4), 56.2 (CH-2), 114.4 (CH-6'), 121.4 (CH-17), 121.9 (CH-12), 122.6 (CH-2'), 124.2 (CH-2''), 128.7 (C-3'), 131.3 (C-1'), 132.7 (C-3''), 133.3 (C-13), 134.0 (C-18), 143.4 (C-4'), 145.3 (C-5'), 211.0 (C-9)

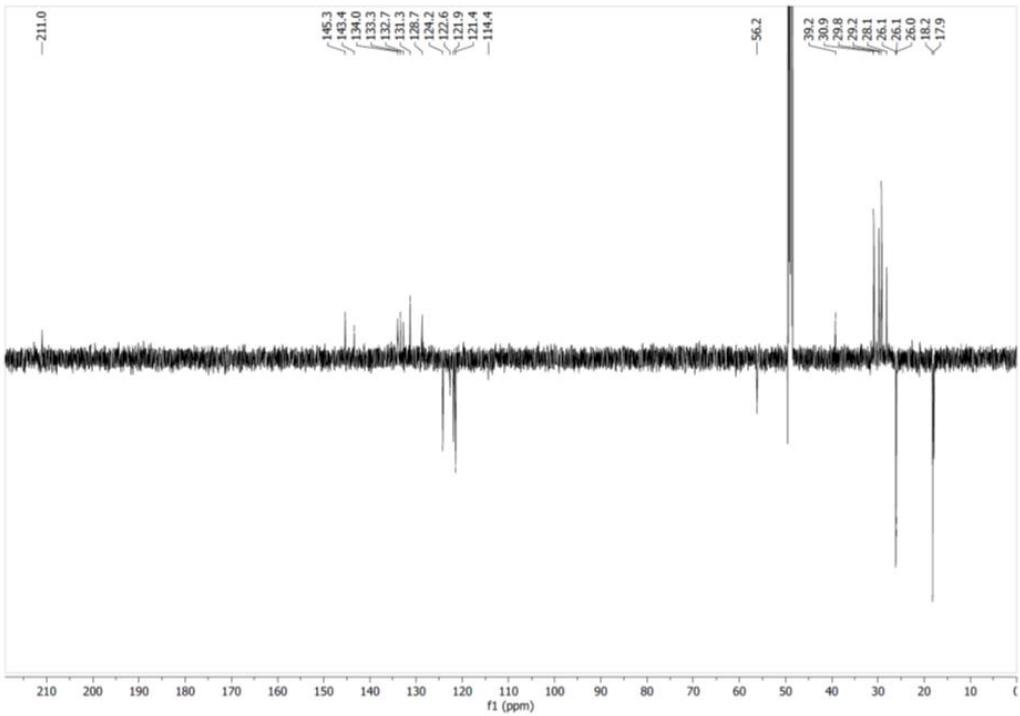
**Supplementary Figures S5.2.59–S5.2.64.**



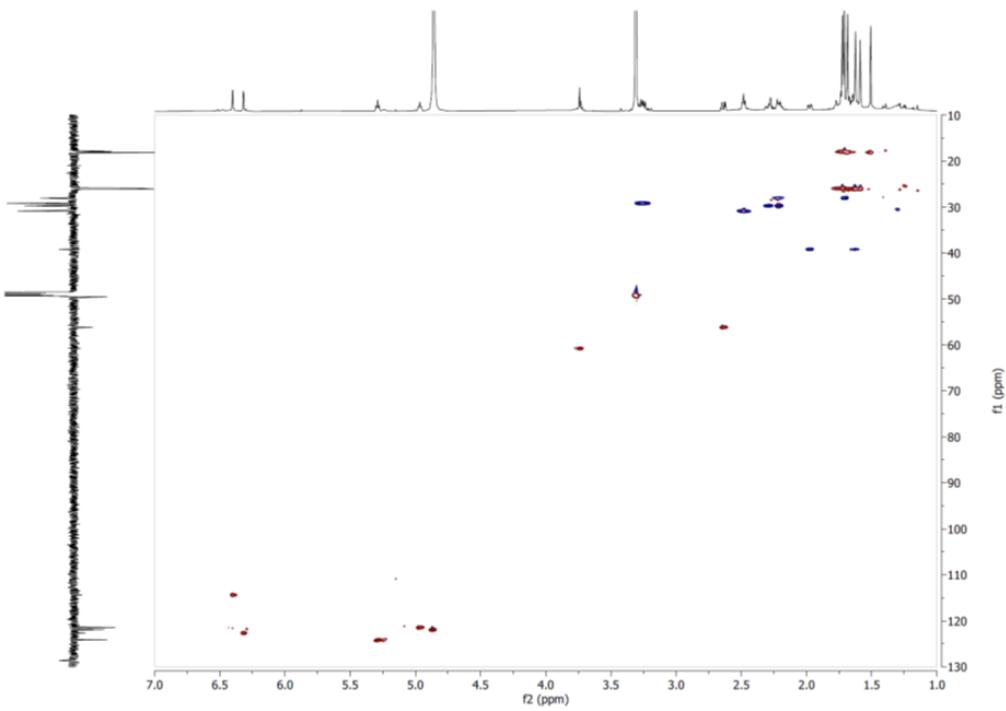
Supplementary Figure S5.2.59.  $^1\text{H}$  NMR spectrum of compound 10 in  $\text{CD}_3\text{OD}$  at 600 MHz



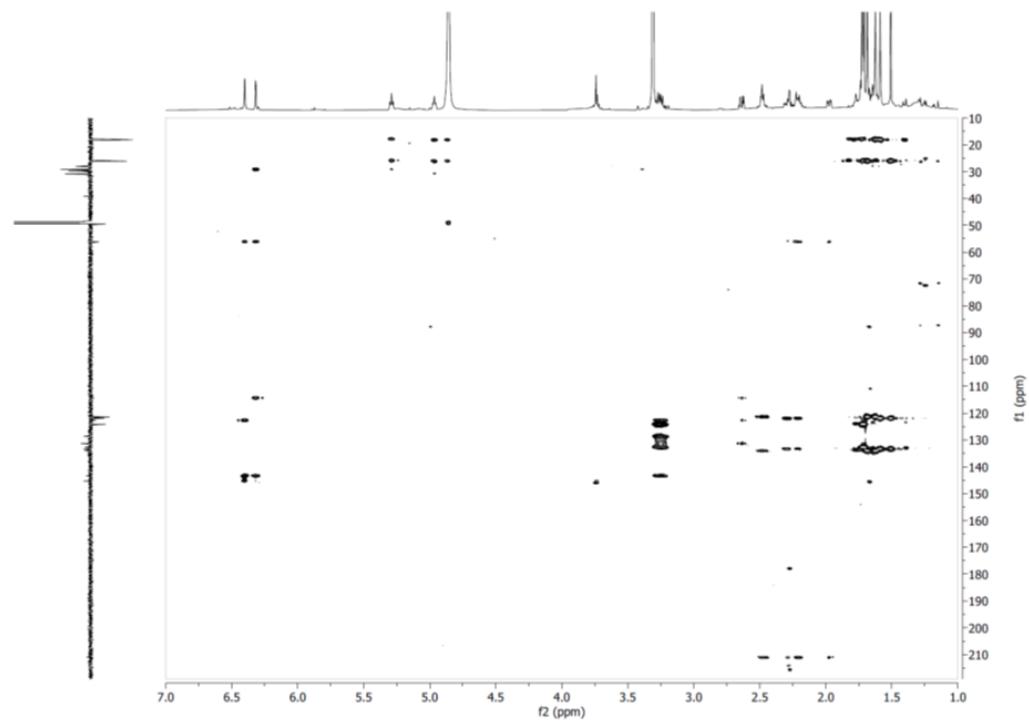
Supplementary Figure S5.2.60. COSY NMR spectrum of compound 10 in  $\text{CD}_3\text{OD}$



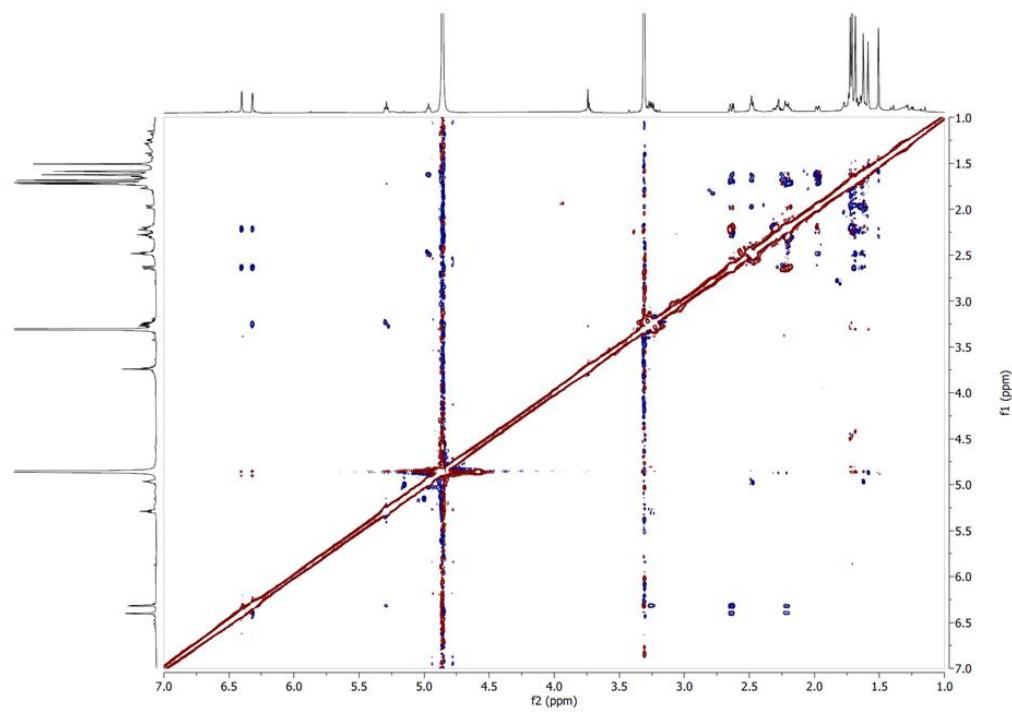
Supplementary Figure S5.2.61. <sup>13</sup>C-DEPTQ NMR spectrum of compound 10 in CD<sub>3</sub>OD at 151 MHz



Supplementary Figure S5.2.62. Edited HSQC NMR spectrum of compound 10 in CD<sub>3</sub>OD

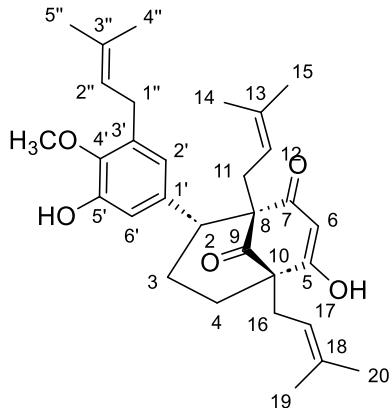


Supplementary Figure S5.2.63. HMBC NMR spectrum of compound 10 in  $\text{CD}_3\text{OD}$



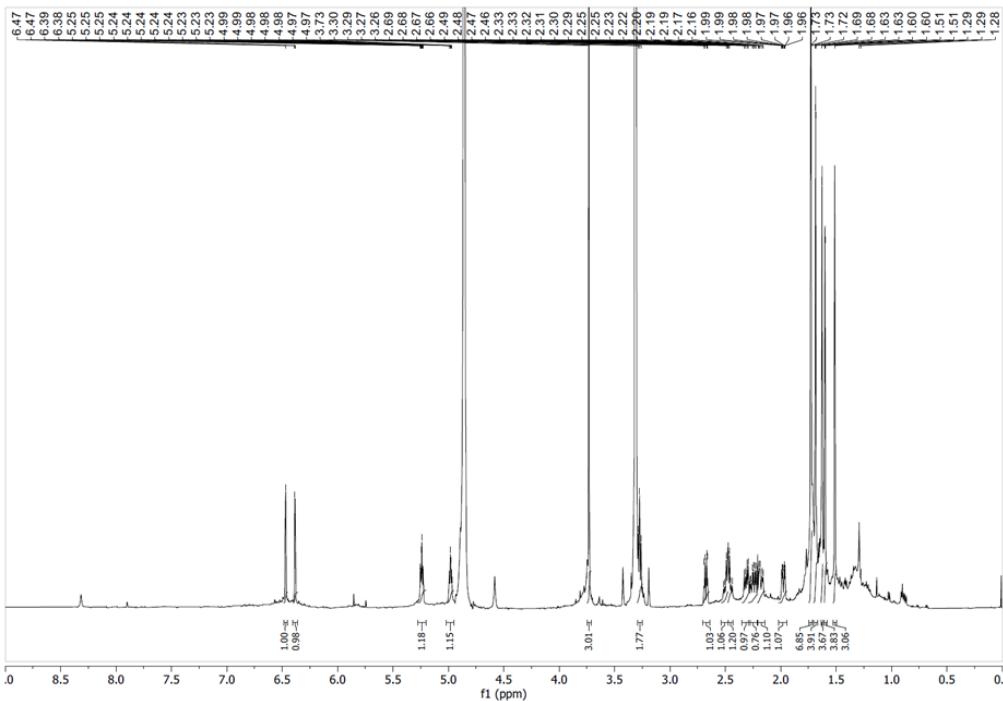
Supplementary Figure S5.2.64. ROESY NMR spectrum of compound 10 in  $\text{CD}_3\text{OD}$

Compound **11** (Hymenotamayonin D): (*2R,8R,10R*)-2-(5-hydroxy-4-methoxy-3-(3-methylbut-2-en-1-yl)phenyl)-5-hydroxy-8,10-bis(3-methylbut-2-en-1-yl)bicyclo[3.3.1]non-6-ene-7,9-dione. Amorphous pale yellow powder, HRESIMS *m/z* 493.2947 [M+H]<sup>+</sup> (calculated for C<sub>31</sub>H<sub>41</sub>O<sub>5</sub>, error -0.28 ppm); [α]<sub>D</sub><sup>20</sup> -27 (c 0.0008, MeOH); UV (c 0.0008, MeOH) λ<sub>max</sub> 207, 286 nm.

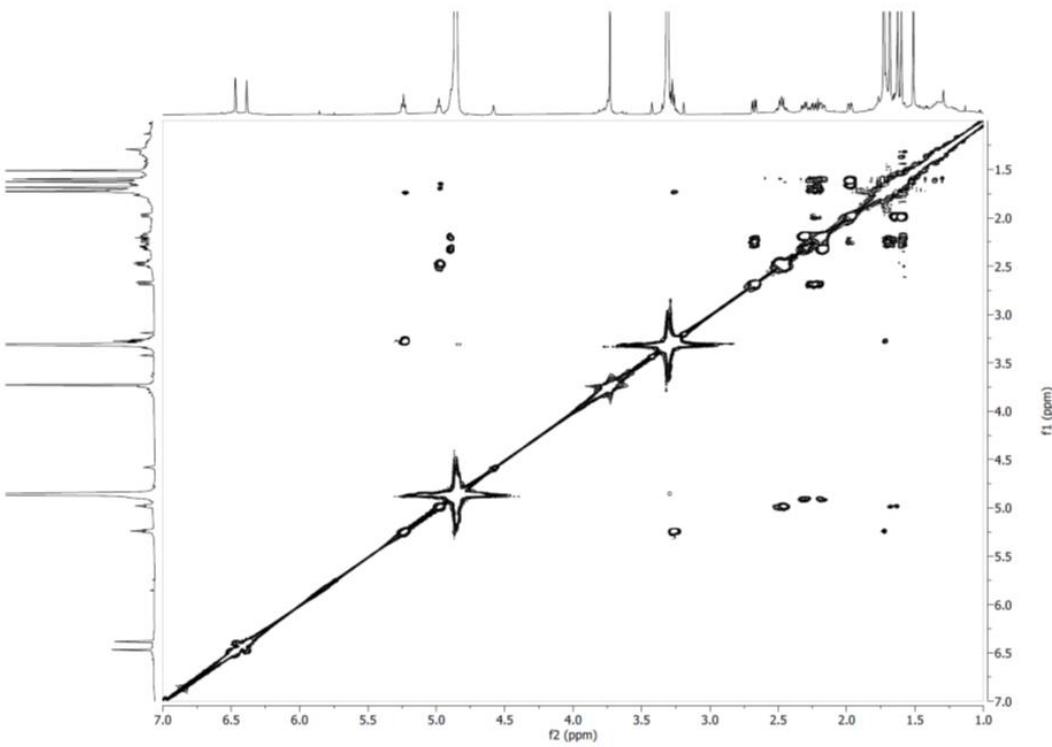


Chemical Formula: C<sub>31</sub>H<sub>40</sub>O<sub>5</sub>  
Exact Mass: 492.29

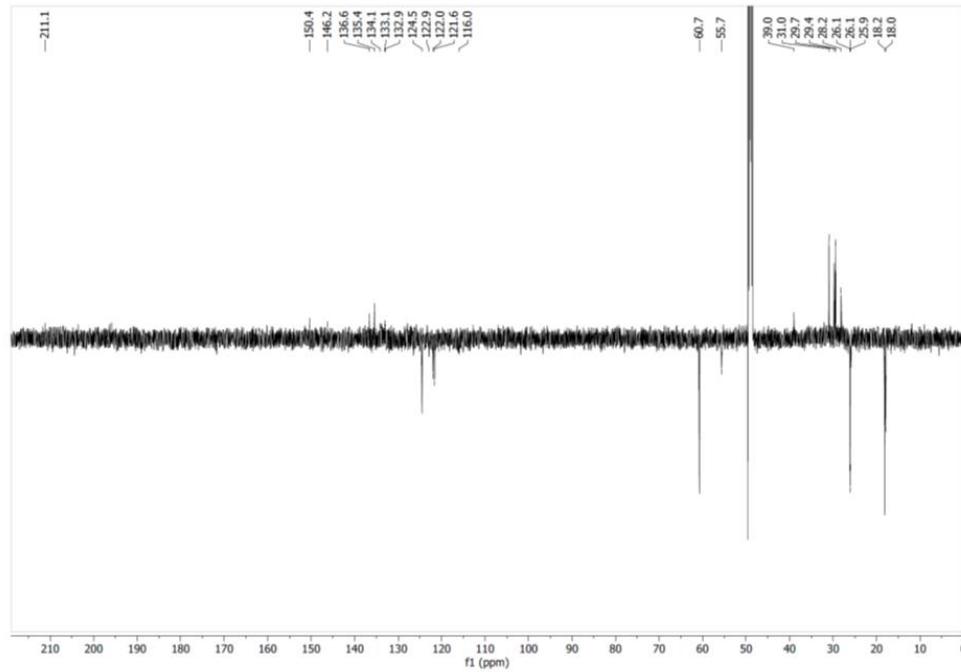
<sup>1</sup>H NMR (CD<sub>3</sub>OD, 600 MHz) δ 1.51 (3H, d, *J* = 1.6 Hz, H<sub>3</sub>-14), 1.60 (3H, d, *J* = 1.6 Hz, H<sub>3</sub>-15), 1.63 (3H, d, *J* = 1.3 Hz, H<sub>3</sub>-20), 1.63 (1H, overlapped, H-4ax), 1.69 (3H, d, *J* = 1.3 Hz, H<sub>3</sub>-19), 1.71 (1H, overlapped, H-3eq), 1.73 (6H, d, *J* = 1.3 Hz, H<sub>3</sub>-4'', H<sub>3</sub>-5''), 1.98 (1H, ddd, *J* = 12.9, 4.8, 1.8 Hz, H-4eq), 2.18 (1H, dd, *J* = 14.9, 7.2 Hz, H-11b), 2.25 (1H, td, *J* = 13.1, 4.8 Hz, H-3ax), 2.32 (1H, dd, *J* = 14.9, 7.2 Hz, H-11a), 2.46 (1H, dd, *J* = 14.3, 7.0 Hz, H-16b), 2.50 (1H, dd, *J* = 14.3, 7.0 Hz, 16a), 2.68 (1H, dd, *J* = 13.1, 4.0 Hz, H-2ax), 3.27 (2H, m, H<sub>2</sub>-1''), 3.73 (3H, s, 4'-OCH<sub>3</sub>), 4.89 (1H, overlapped, H-12), 4.98 (1H, thept, *J* = 7.0, 1.6 Hz, H-17), 5.24 (1H, thept, *J* = 7.2, 1.3 Hz, H-2''), 6.38 (1H, d, *J* = 2.2 Hz, H-2'), 6.47 (1H, d, *J* = 2.2 Hz, H-6'); <sup>13</sup>C NMR (MeOD, 151 MHz) δ 18.0 (CH<sub>3</sub>-4''), 18.2 (CH<sub>3</sub>-14, CH<sub>3</sub>-19), 25.9 (CH<sub>3</sub>-5''), 26.1 (CH<sub>3</sub>-15), 26.1 (CH<sub>3</sub>-20), 28.2 (CH<sub>2</sub>-3), 29.4 (CH<sub>2</sub>-1''), 29.7 (CH<sub>2</sub>-11), 31.0 (CH<sub>2</sub>-16), 39.0 (CH<sub>2</sub>-4), 55.7 (CH-2), 60.7 (4'-OCH<sub>3</sub>), 116.0 (CH-6'), 121.6 (CH-17), 122.0 (CH-12), 122.9 (CH-2'), 124.5 (CH-2''), 132.9 (C-3''), 133.1 (C-13), 134.1 (C-18), 135.4 (C-3'), 136.6 (C-1'), 146.2 (C-4'), 150.4 (C-5'), 211.1 (C-9). Supplementary Figures S5.2.65-S5.2.70.



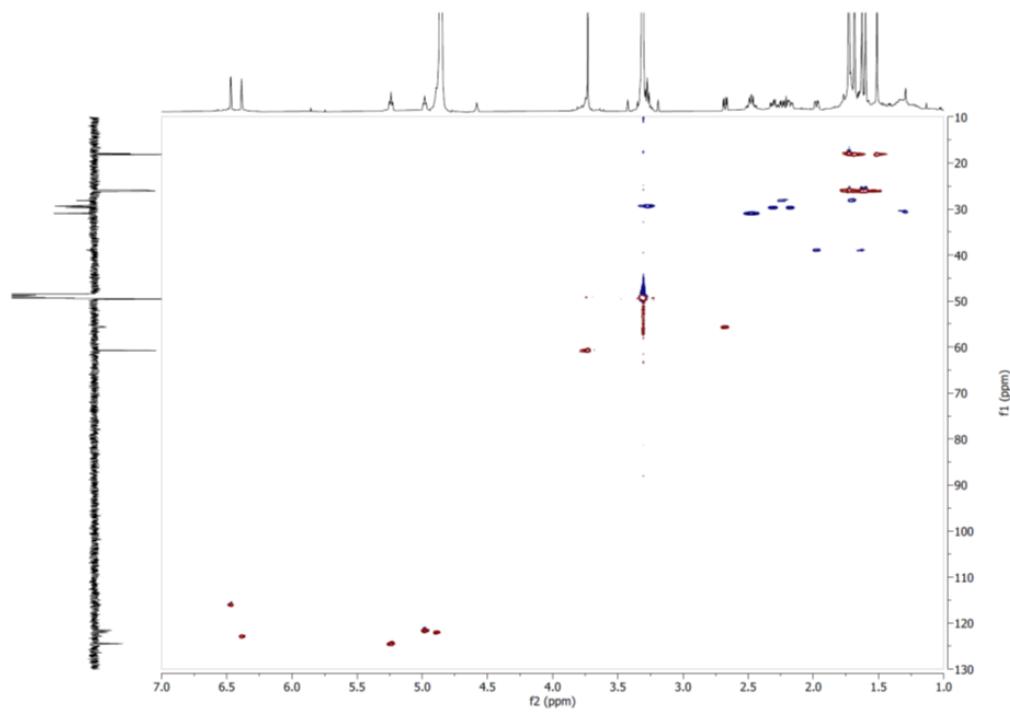
Supplementary Figure S5.2.65.  $^1\text{H}$  NMR spectrum of compound 11 in  $\text{CD}_3\text{OD}$  at 600 MHz



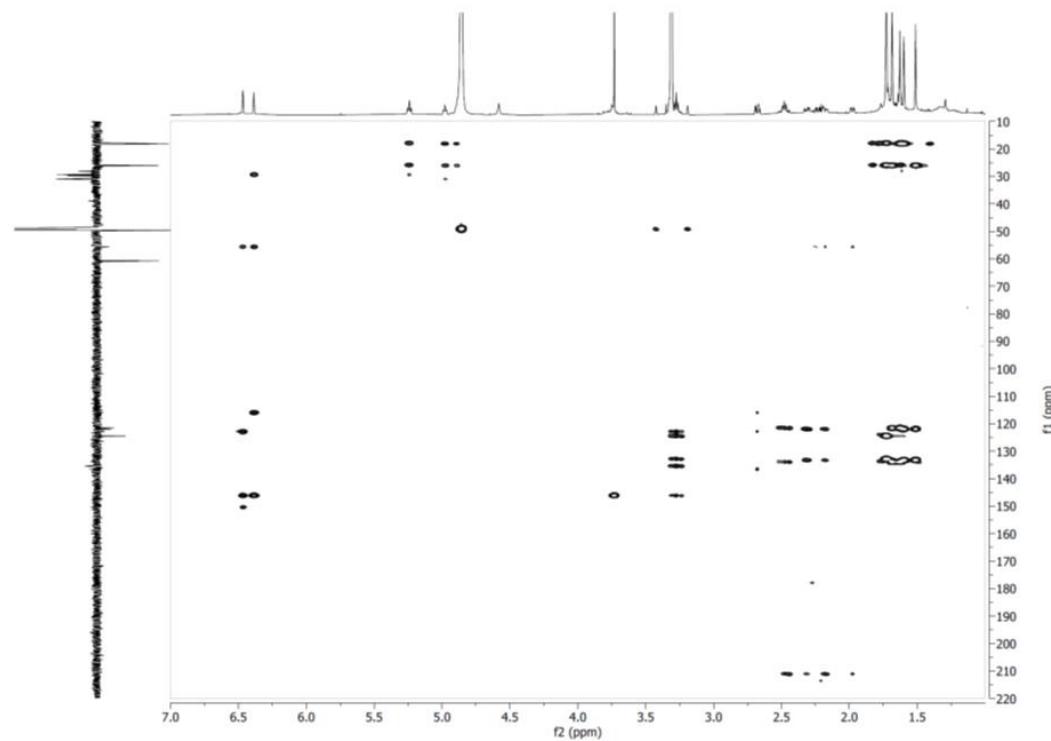
Supplementary Figure S5.2.66. COSY NMR spectrum of compound 11 in  $\text{CD}_3\text{OD}$



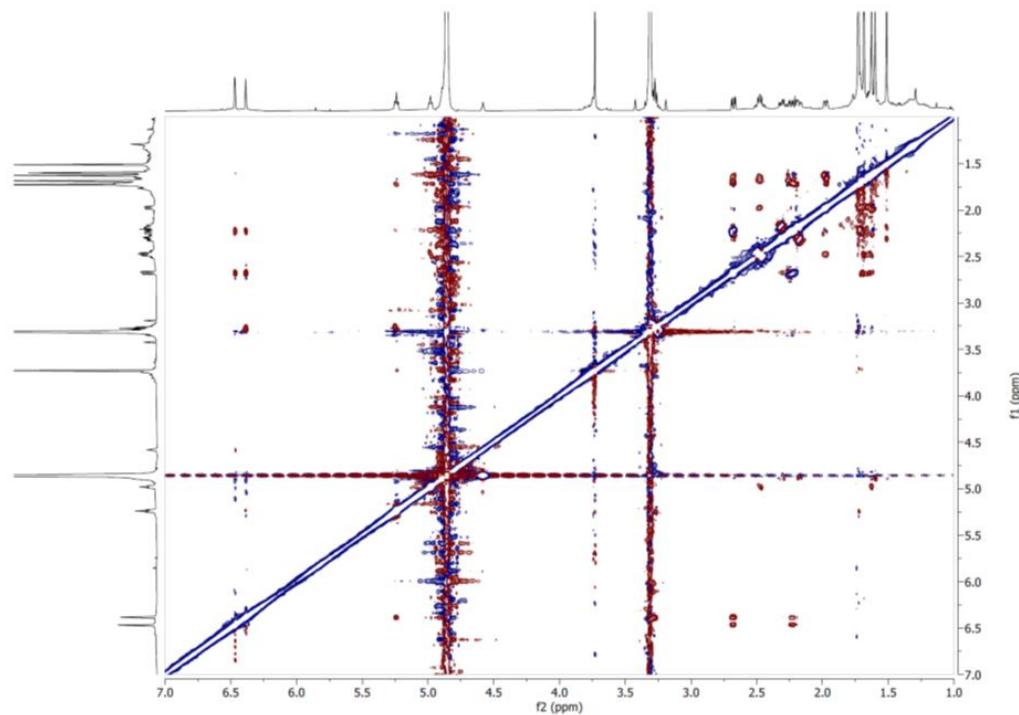
Supplementary Figure S5.2.67.  $^{13}\text{C}$ -DEPTQ NMR spectrum of compound 11 in  $\text{CD}_3\text{OD}$  at 151 MHz



Supplementary Figure S5.2.68. Edited HSQC NMR spectrum of compound 11 in  $\text{CD}_3\text{OD}$

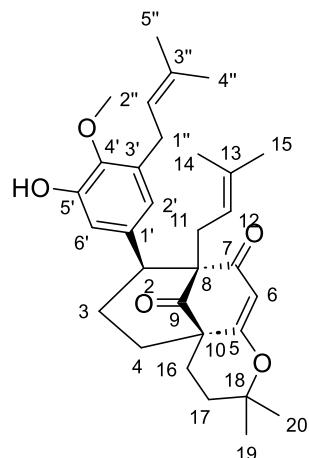


Supplementary Figure S5.2.69. HMBC NMR spectrum of compound 11 in  $\text{CD}_3\text{OD}$



Supplementary Figure S5.2.70. ROESY NMR spectrum of compound 11 in  $\text{CD}_3\text{OD}$

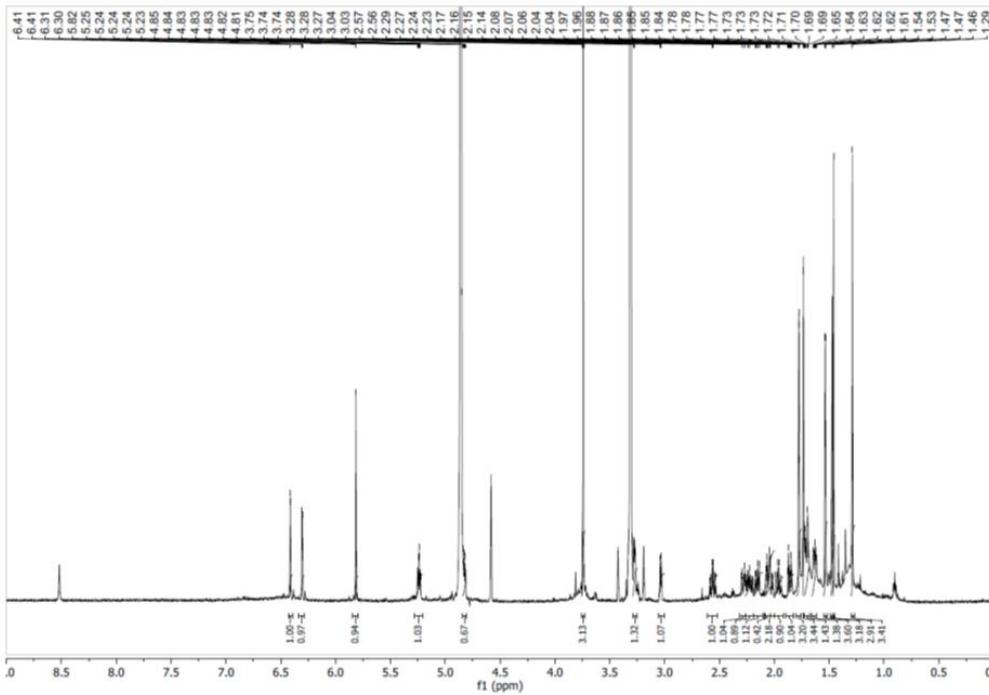
Compound **12** (Hymenotamayonin F): (2*S*,8*R*,10*R*)-2-(5-hydroxy, 4-methoxy-3-(3-methylbut-2-en-1-yl)phenyl)-18,18-dimethyl-8-(3-methylbut-2-en-1-yl)-5-oxotricyclo[7.3.1.0<sup>5,10</sup>]dodec-5-ene-7,9-dione. Amorphous pale yellow powder, HRESIMS *m/z* 493.2747 [M+H]<sup>+</sup> (calculated for C<sub>31</sub>H<sub>41</sub>O<sub>5</sub>, error -0.16 ppm); [α]<sub>D</sub><sup>20</sup> +6 (c 0.0004, MeOH); UV (c 0.0004, MeOH) λ<sub>max</sub> 205, 273 nm.



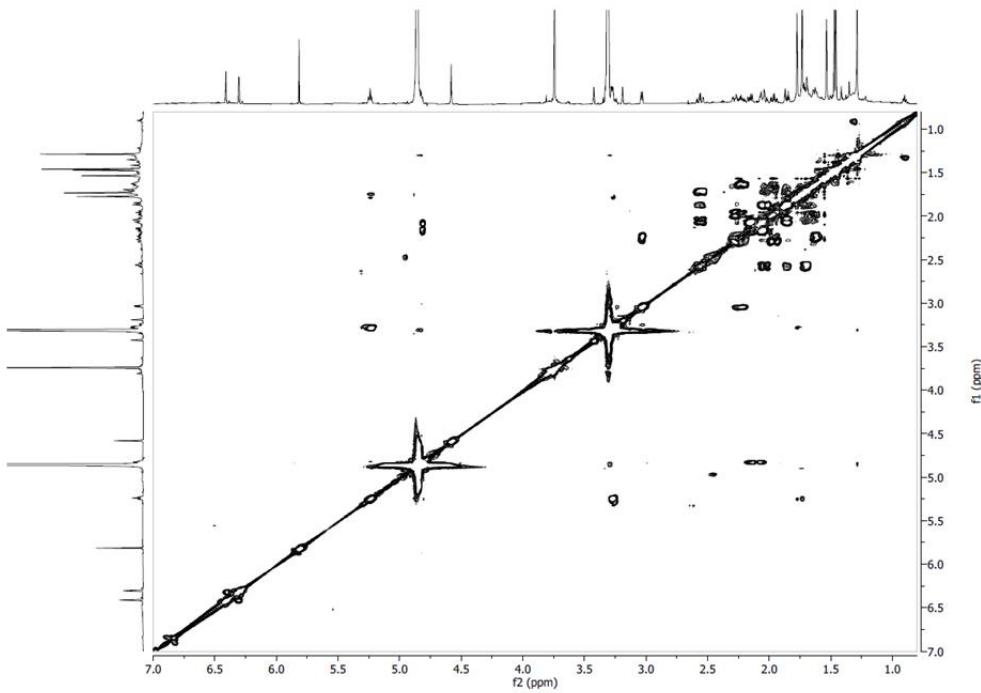
Chemical Formula: C<sub>31</sub>H<sub>40</sub>O<sub>5</sub>

Exact Mass: 492.29

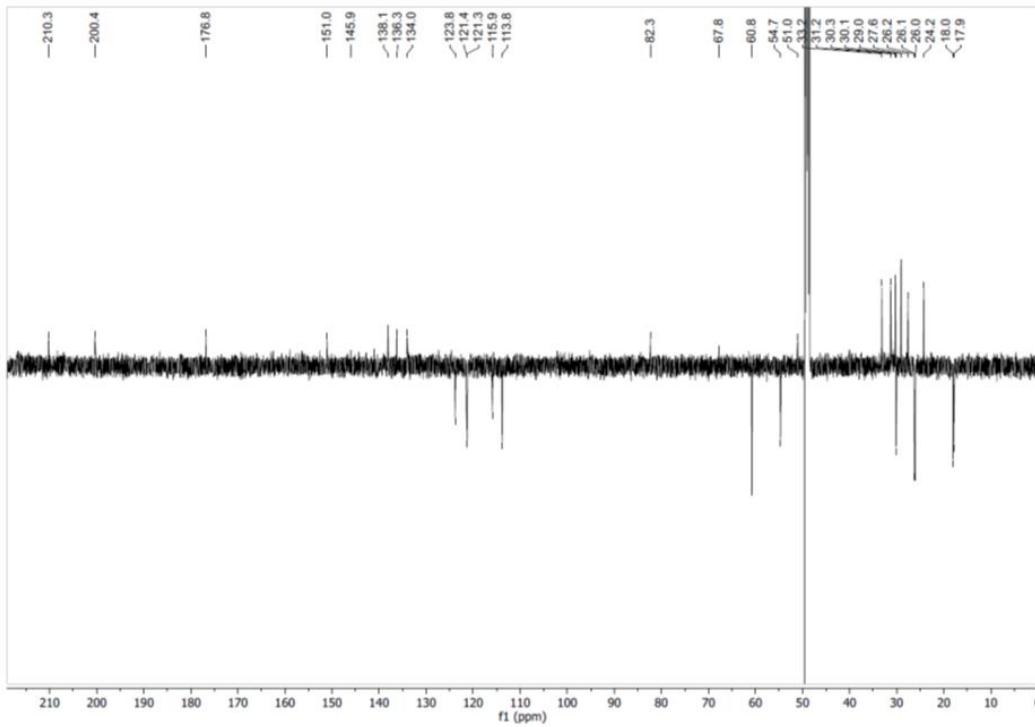
<sup>1</sup>H NMR (CD<sub>3</sub>OD, 600 MHz) δ 1.29 (3H, s, H<sub>3</sub>-20), 1.46 (3H, s, H<sub>3</sub>-19), 1.47 (3H, d, *J* = 1.3 Hz, H<sub>3</sub>-14), 1.54 (3H, d, *J* = 1.3 Hz, H<sub>3</sub>-15), 1.63 (1H, m, H-3eq), 1.71 (1H, dt, *J* = 14.4, 4.2 Hz, H-16eq), 1.73 (3H, d, *J* = 1.3 Hz, H<sub>3</sub>-4''), 1.78 (3H, d, *J* = 1.3 Hz, H<sub>3</sub>-5''), 1.86 (1H, dt, *J* = 14.3, 4.1 Hz, H-17eq), 1.96 (1H, td, *J* = 13.3, 4.5 Hz, H-4ax), 2.04 (1H, td, *J* = 14.3, 4.1 Hz, H-17ax), 2.06 (1H, dd, *J* = 14.7, 6.1 Hz, H-11b), 2.16 (1H, dd, *J* = 14.7, 7.8 Hz, H-11a), 2.23 (1H, m, H-3ax), 2.28 (1H, dd, *J* = 13.3, 4.5 Hz, H-4eq), 2.56 (1H, td, *J* = 14.4, 4.2 Hz, H-16ax), 3.04 (1H, d, *J* = 6.2 Hz, H-2eq), 3.28 (2H, m, H<sub>2</sub>-1''), 3.74 (3H, s, 4'-OCH<sub>3</sub>), 4.83 (1H, thept, *J* = 7.6, 1.3 Hz, H-12), 5.24 (1H, thept, *J* = 7.5, 1.3 Hz, H-2''); <sup>13</sup>C NMR (CD<sub>3</sub>OD, 151 MHz) δ 17.9 (CH<sub>3</sub>-14), 18.0 (CH<sub>3</sub>-4''), 24.2 (CH<sub>2</sub>-16), 26.0 (CH<sub>3</sub>-15), 26.1 (CH<sub>3</sub>-5''), 26.2 (CH<sub>3</sub>-20), 27.6 (CH<sub>2</sub>-3), 29.0 (CH<sub>2</sub>-1''), 30.1 (CH<sub>3</sub>-19), 30.3 (CH<sub>2</sub>-11), 31.2 (CH<sub>2</sub>-17), 33.2 (CH<sub>2</sub>-4), 51.0 (C-10), 54.7 (CH-2), 60.8 (4'-OCH<sub>3</sub>), 67.8 (C-8), 82.3 (C-18), 113.8 (CH-6), 115.9 (CH-6''), 121.3 (CH-12), 121.4 (CH-2''), 123.8 (CH-2''), 134.0 (C-3''), 136.3 (C-3''), 138.1 (C-1''), 145.9 (C-4''), 151.0 (C-5''), 176.8 (C-5), 200.4 (C-7), 210.3 (C-9). Supplementary Figures S5.2.71-S5.2.76.



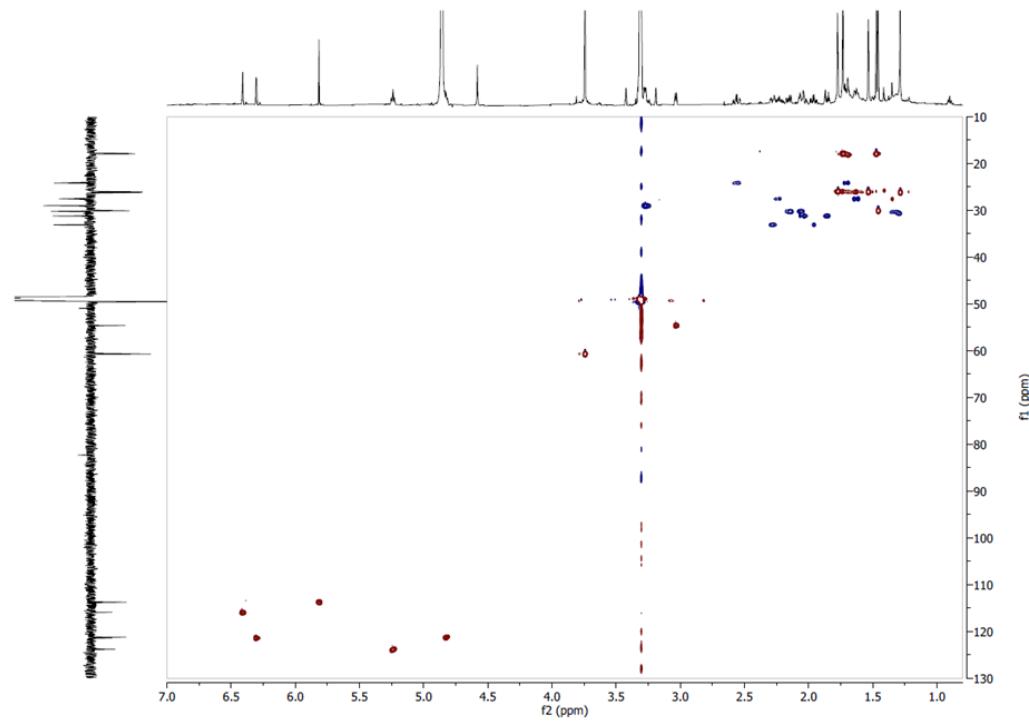
Supplementary Figure S5.2.71.  $^1\text{H}$  NMR spectrum of compound 12 in  $\text{CD}_3\text{OD}$  at 600 MHz



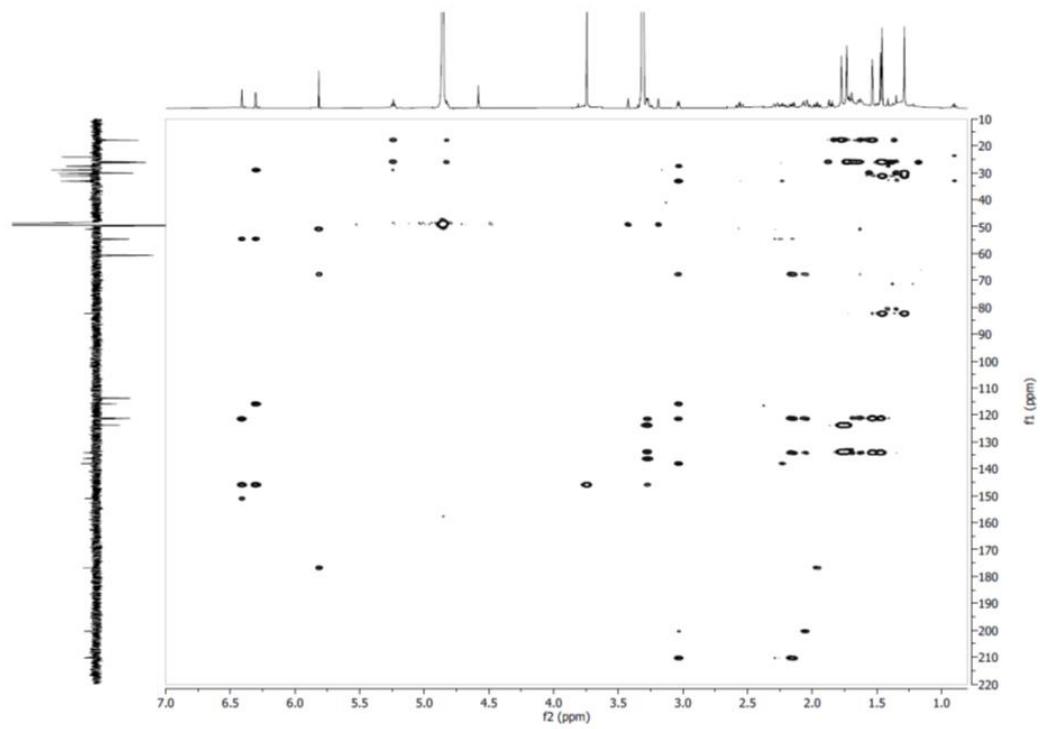
Supplementary Figure S5.2.72. COSY NMR spectrum of compound 12 in  $\text{CD}_3\text{OD}$



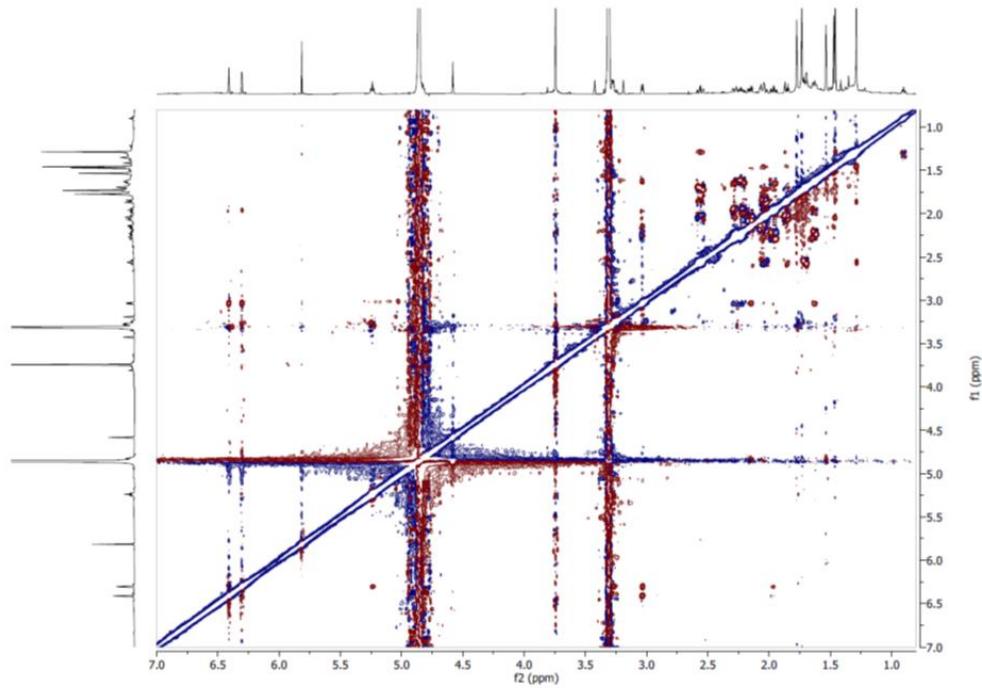
Supplementary Figure S5.2.73.  $^{13}\text{C}$ -DEPTQ NMR spectrum of compound 12 in  $\text{CD}_3\text{OD}$  at 151 MHz



Supplementary Figure S5.2.74. Edited HSQC NMR spectrum of compound 12 in  $\text{CD}_3\text{OD}$

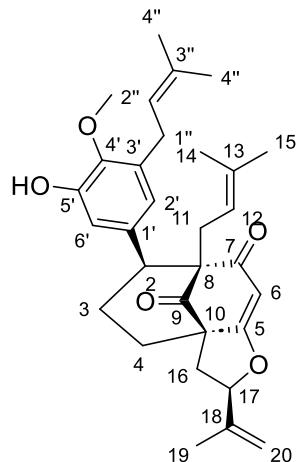


Supplementary Figure S5.2.75. HMBC NMR spectrum of compound 12 in  $\text{CD}_3\text{OD}$



Supplementary Figure S5.2.76. ROESY NMR spectrum of compound 12 in  $\text{CD}_3\text{OD}$

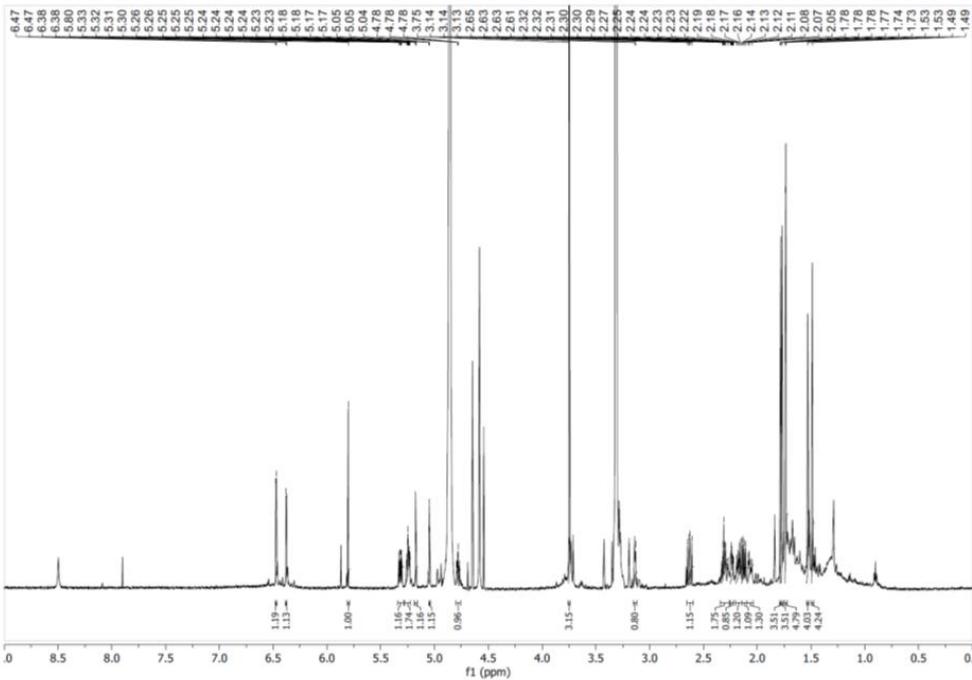
Compound **13** (Hymenotamayonin E): (*2S,8R,10R,17R*)-2-(5-hydroxy, 4-methoxy-3-(3-methylbut-2-en-1-yl)phenyl)-8-(3-methylbut-2-en-1-yl)-17-(prop-1-en-2-yl-5-oxotricyclo[6.3.1.0<sup>5,10</sup>]dodec-5-ene-7,9-dione. Amorphous pale yellow powder, HRESIMS *m/z* 491.2792 [M+H]<sup>+</sup> (calculated for C<sub>31</sub>H<sub>39</sub>O<sub>5</sub>, error 0.08 ppm); [α]<sub>D</sub><sup>20</sup> +0.4 (c 0.0005, MeOH); UV (c 0.0005, MeOH) λ<sub>max</sub> 204, 270 nm.



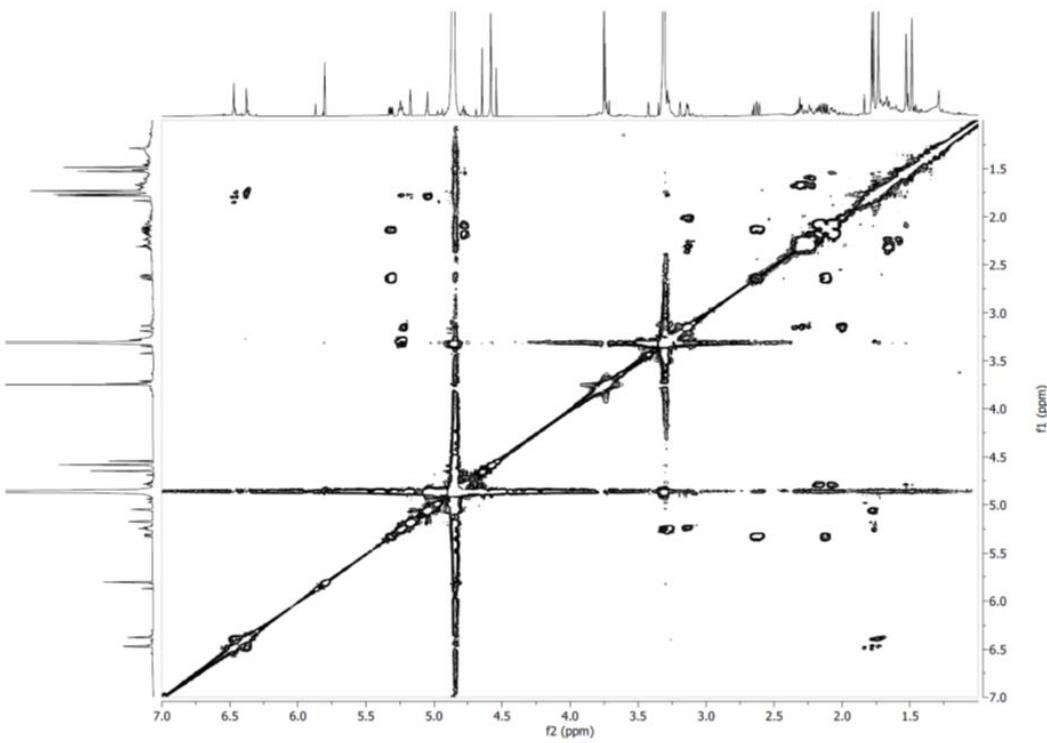
Chemical Formula: C<sub>31</sub>H<sub>38</sub>O<sub>5</sub>

Exact Mass: 490.27

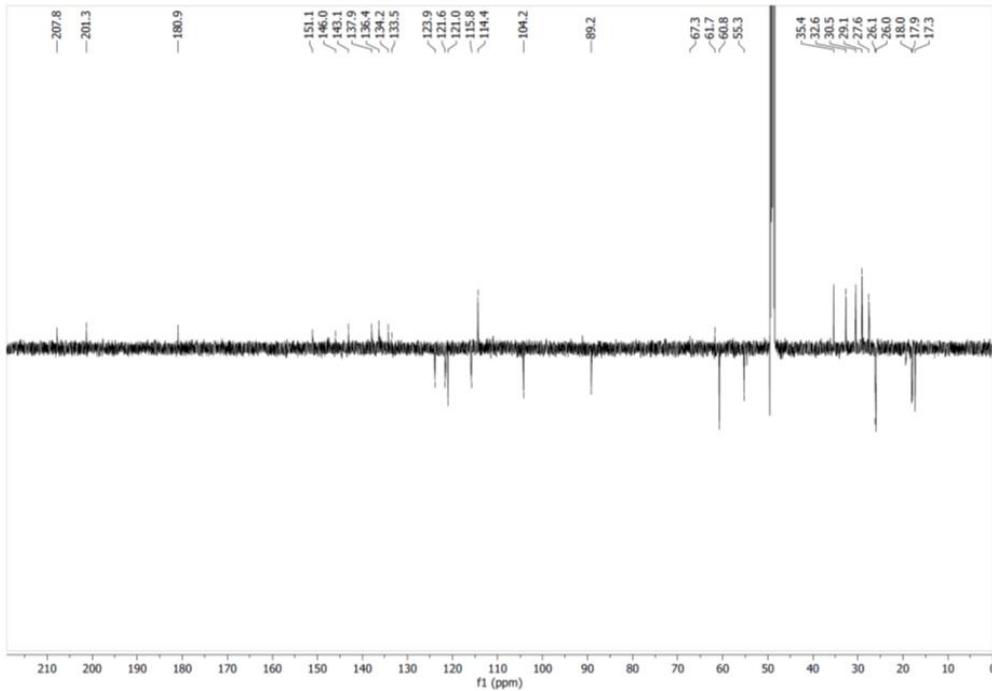
<sup>1</sup>H NMR (CD<sub>3</sub>OD, 600 MHz) δ 1.49 (3H, d, *J* = 1.4 Hz, H<sub>3</sub>-14), 1.53 (3H, d, *J* = 1.4 Hz, H<sub>3</sub>-15), 1.66 (1H, m, H-3eq), 1.73 (3H, d, *J* = 1.3 Hz, H<sub>3</sub>-4<sup>11</sup>), 1.77 (3H, d, *J* = 1.3 Hz, H<sub>3</sub>-5<sup>11</sup>), 1.78 (3H, t, *J* = 1.2 Hz, H<sub>3</sub>-19), 2.07 (1H, dd, *J* = 14.5, 6.0 Hz, H-11b), 2.12 (1H, dd, *J* = 13.0, 5.4 Hz, H-16b), 2.17 (1H, dd, *J* = 14.5, 7.7 Hz, H-11a), 2.23 (1H, brd, *J* = 9.4 Hz, H-4eq), 2.30 (1H, overlapped, H-4ax), 2.32 (1H, overlapped, H-3ax), 2.63 (1H, dd, *J* = 13.0, 11.2 Hz, 16a), 3.14 (1H, d, *J* = 3.8 Hz, H-2eq), 3.75 (3H, s, 4'-OCH<sub>3</sub>), 4.78 (1H, ddhept, *J* = 7.7, 6.0, 1.4 Hz, H-12), 5.05 (1H, p, *J* = 1.2 Hz, 20b), 5.17 (1H, q, *J* = 1.2 Hz, 20a), 5.25 (2H, thept, *J* = 7.5, 1.3 Hz, 2<sup>11</sup>), 5.32 (1H, dd, *J* = 11.2, 5.4 Hz, H-17), 5.80 (1H, s, H-6), 6.38 (1H, d, *J* = 2.3 Hz, H-2<sup>1</sup>), 6.47 (1H, d, *J* = 2.3 Hz, H-6<sup>1</sup>); <sup>13</sup>C NMR (CD<sub>3</sub>OD, 151 MHz) δ 17.3 (CH<sub>3</sub>-19), 17.9 (CH<sub>3</sub>-14), 18.0 (CH<sub>3</sub>-4<sup>11</sup>), 26.0 (CH<sub>3</sub>-15), 26.1 (CH<sub>3</sub>-5<sup>11</sup>), 27.6 (CH<sub>2</sub>-3), 29.1 (CH<sub>2</sub>-1<sup>11</sup>), 30.5 (CH<sub>2</sub>-11), 32.6 (CH<sub>2</sub>-4), 35.4 (CH<sub>2</sub>-16), 55.3 (CH-2), 60.8 (4'-OCH<sub>3</sub>), 61.7 (C-10), 67.3 (C-8), 89.2 (CH-17), 104.2 (CH-6), 114.4 (CH<sub>2</sub>-20), 115.8 (CH-6<sup>1</sup>), 121.0 (CH-12), 121.6 (CH-2<sup>1</sup>), 123.9 (CH-2<sup>11</sup>), 133.5 (C-3<sup>11</sup>), 134.2 (C-13), 136.4 (C-3<sup>1</sup>), 137.9 (C-1<sup>1</sup>), 143.1 (C-18), 146.0 (C-4<sup>1</sup>), 151.1 (C-5<sup>1</sup>), 180.9 (C-5), 201.3 (C-7), 207.8 (C-9). Supplementary Figures S5.2.77-S5.2.82.



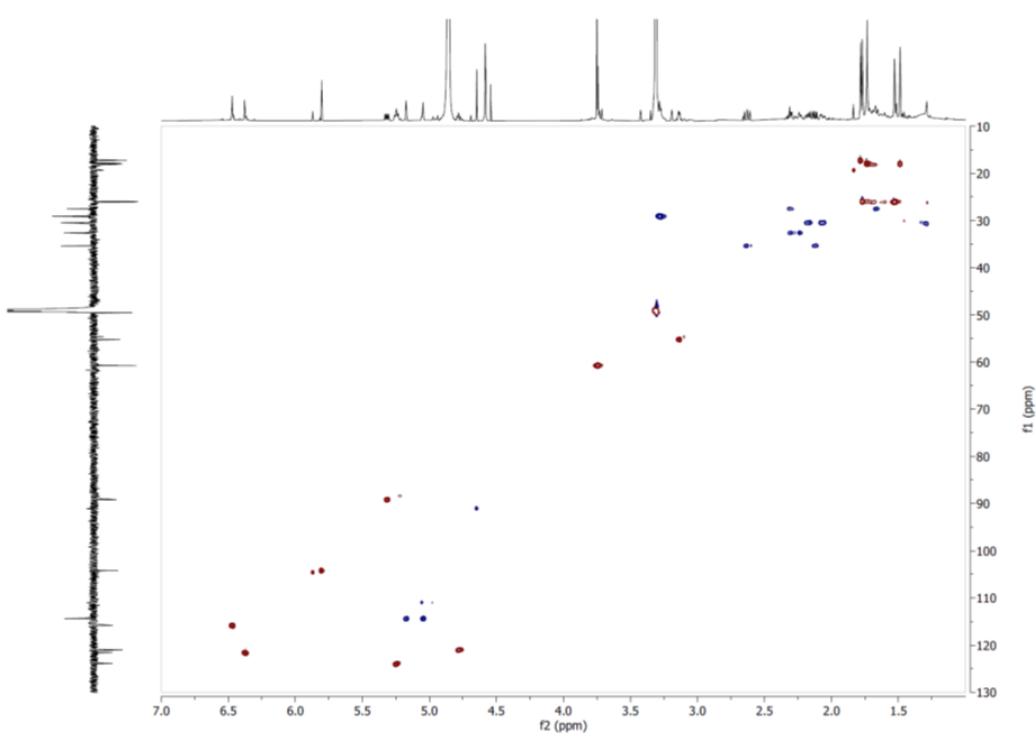
Supplementary Figure S5.2.77.  $^1\text{H}$  NMR spectrum of compound 13 in  $\text{CD}_3\text{OD}$  at 600 MHz



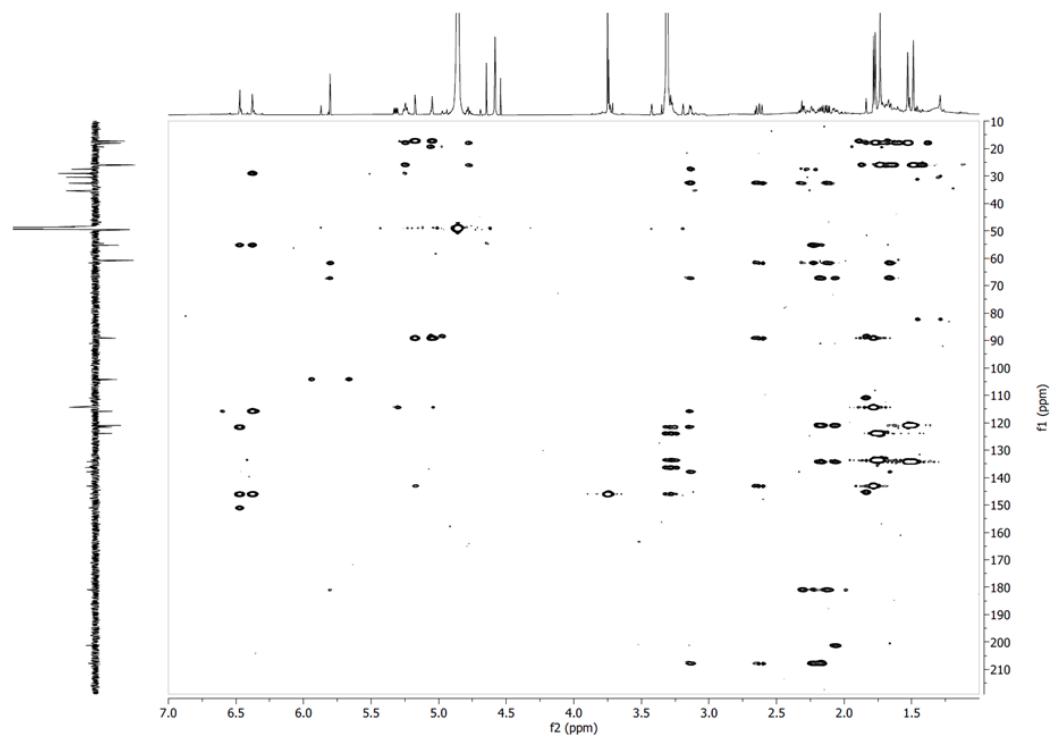
Supplementary Figure S5.2.78. COSY NMR spectrum of compound 13 in  $\text{CD}_3\text{OD}$



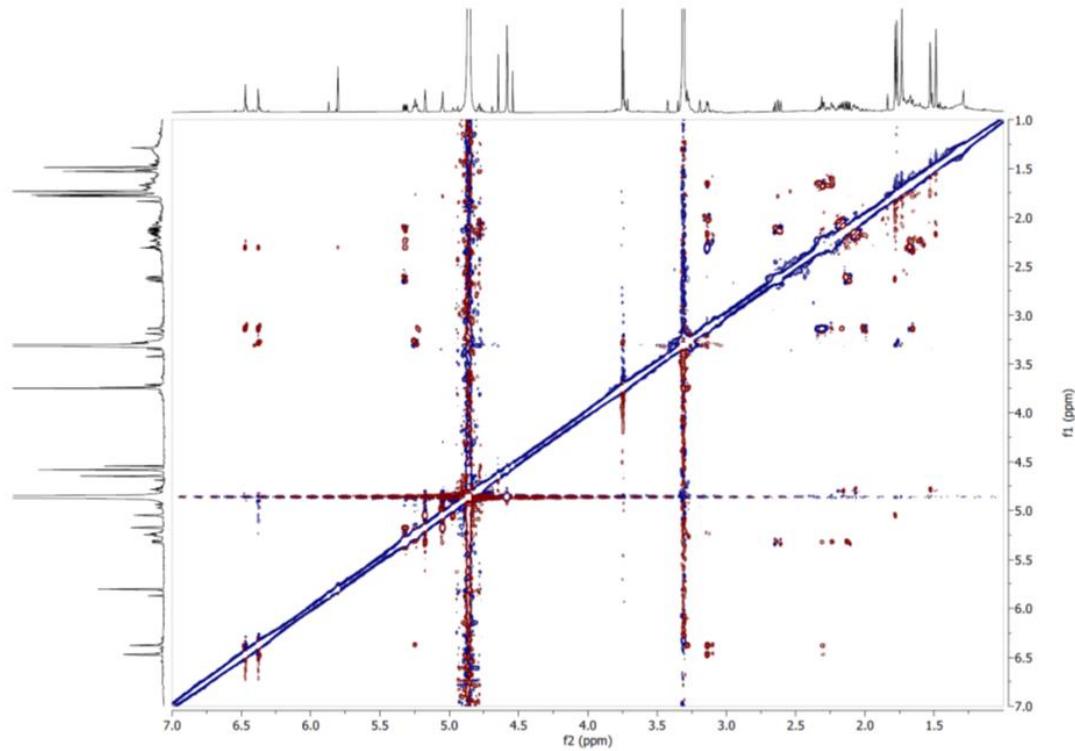
Supplementary Figure S5.2.79.  $^{13}\text{C}$ -DEPTQ NMR spectrum of compound 13 in  $\text{CD}_3\text{OD}$  at 151 MHz



Supplementary Figure S5.2.80. Edited HSQC NMR spectrum of compound 13 in  $\text{CD}_3\text{OD}$



Supplementary Figure S5.2.81. HMBC NMR spectrum of compound 13 in  $\text{CD}_3\text{OD}$



Supplementary Figure S5.2.82. ROESY NMR spectrum of compound 13 in  $\text{CD}_3\text{OD}$