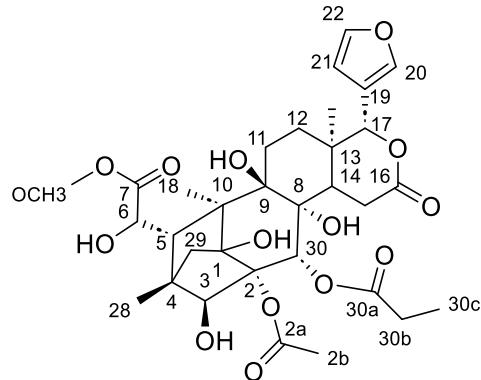


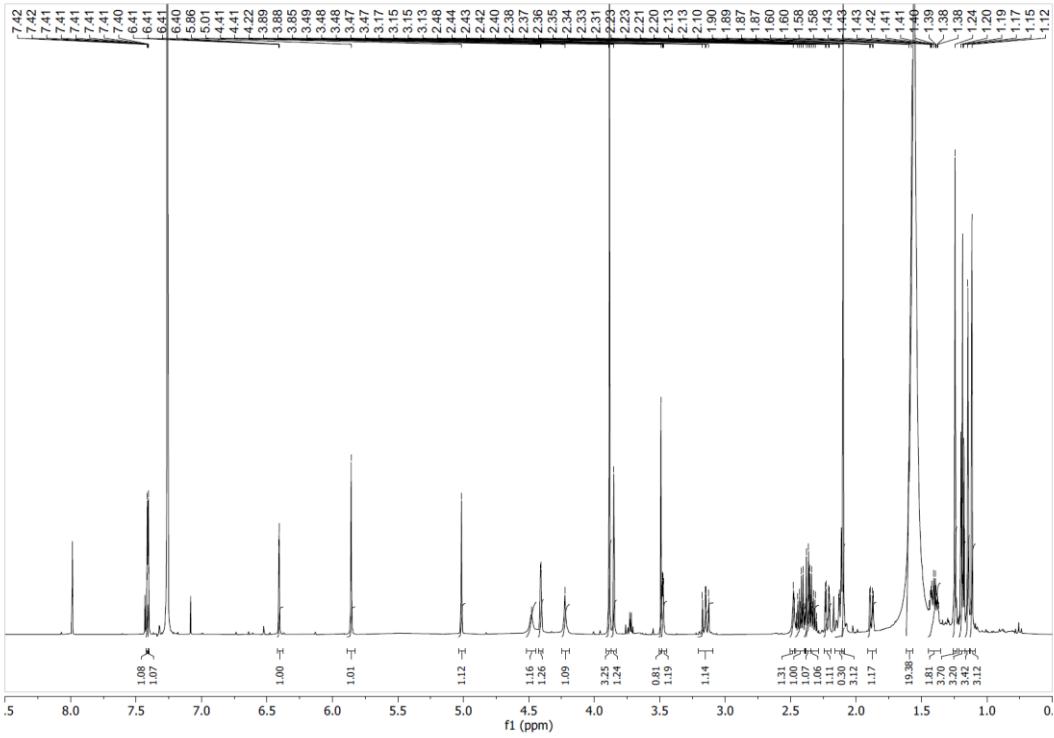
Description of the Compound Isolated.

Compound **1**. Amorphous white powder, HRESIMS m/z 673.2457 [M+Na]⁺ (calculated for C₃₂H₄₂O₁₄Na, error -1.40 ppm), 649.2477 [M-H]⁻ (calculated for C₃₂H₄₁O₁₄, error -2.06 ppm); $[\alpha]_D^{20}$ -0.9 (c 0.0005 CHCl₃); UV (c 0.0005, MeOH) λ_{max} 203, 217 nm (s).

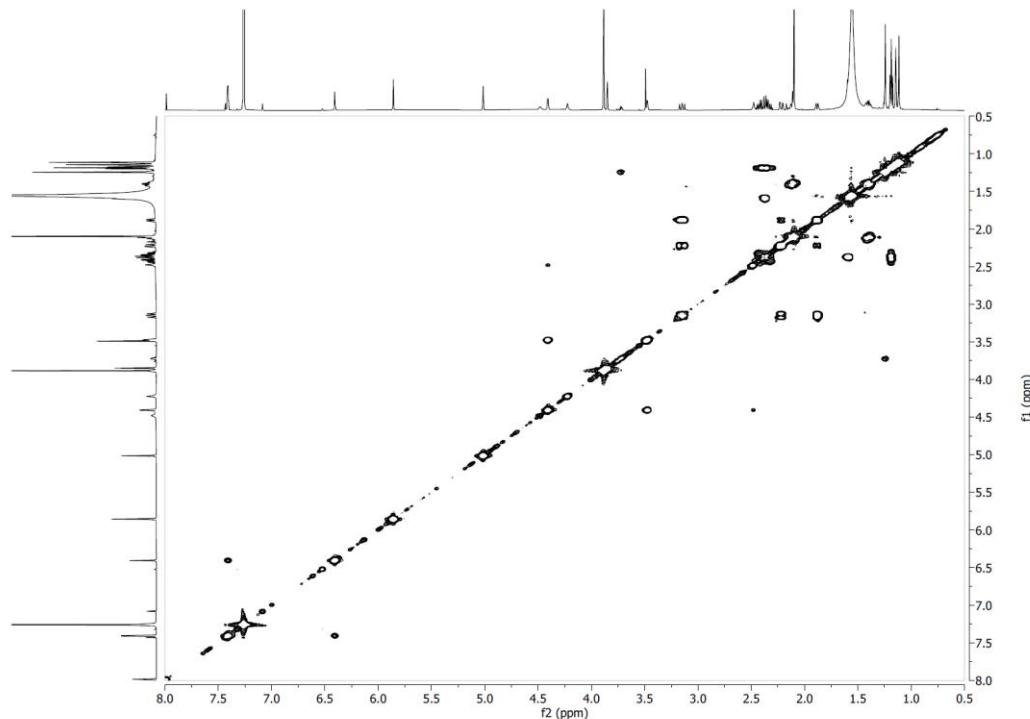


Chemical Formula: C₃₂H₄₂O₁₄
Exact Mass: 650.26

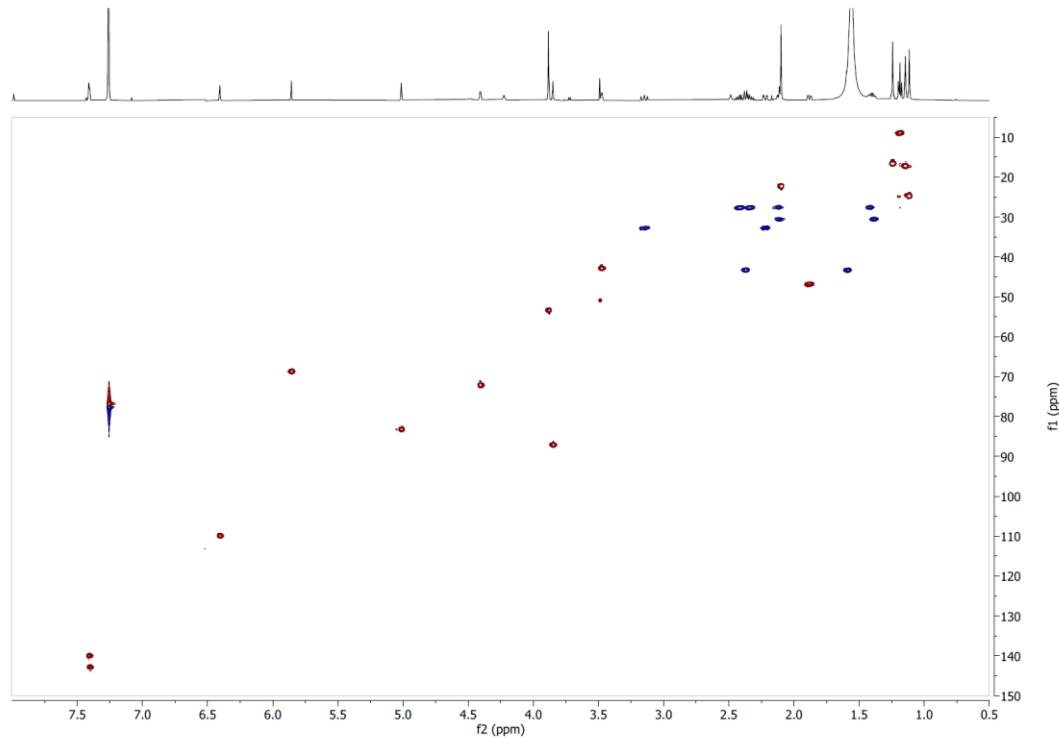
¹H NMR (CDCl₃, 600 MHz) δ 1.12 (3H, s, H₃-18), 1.15 (3H, s, H₃-19), 1.19 (3H, t, J = 7.6 Hz, H₃-30c), 1.24 (3H, s, H₃-28), 1.39 (1H, m, H-11a), 1.41 (1H, m, H-12a), 1.59 (1H, d, J = 10.8 Hz, H-29proR), 1.88 (1H, dd, J = 13.3, 3.3 Hz, H-14), 2.10 (3H, s, H₃-2b), 2.13 (2H, m, H-11b, H-12b), 2.22 (1H, dd, J = 15.5, 3.3 Hz, H-15a), 2.33 (1H, dq, J = 16.7, 7.6 Hz, H-30b'), 2.37 (1H, d, J = 10.8 Hz, H-29 proS), 2.42 (1H, dq, J = 16.7, 7.6 Hz, H-30b'), 2.48 (1H, s, OH-6), 3.15 (1H, dd, J = 15.5, 13.3 Hz, H-15b), 3.48 (1H, d, J = 4.5 Hz, H-5), 3.85 (1H, s, H-3), 3.88 (3H, s, OCH₃), 4.22 (1H, s, OH-9), 4.41 (1H, d, J = 4.5 Hz, H-6), 4.48 (1H, s, OH-3), 5.01 (1H, s, H-17), 5.86 (1H, s, H-30), 6.41 (1H, d, J = 1.7 Hz, H-22), 7.41 (1H, t, J = 1.7 Hz, H-23), 7.41 (1H, d, J = 1.7 Hz, H-21); ¹H NMR (CDCl₃, 600 MHz) δ 8.9 (CH₃-30c), 16.5 (CH₃-28), 17.2 (CH₃-19), 22.3 (CH₃-2b), 24.8 (CH₃-18), 27.6 (CH₂-11, CH₂-30b), 30.5 (CH₂-12), 32.8 (CH₂-15), 36.2 (C-13), 42.9 (CH-5), 43.2 (CH₂-29), 46.8 (CH-14), 53.4 (OCH₃), 68.7 (CH-30), 72.1 (CH-6), 75.8 (C-9), 77.6 (C-8), 83.1 (CH-17), 85.2 (C-2), 86.6 (C-1), 87.2 (CH-3), 109.9 (CH-22), 120.9 (C-20), 139.9 (CH-21), 142.9 (CH-23), 171.0 (C-2a), 174.6 (C-16), 175.5 (C-30a), 176.4 (C-7). Supplementary Figures S4.2.9-S4.2.13



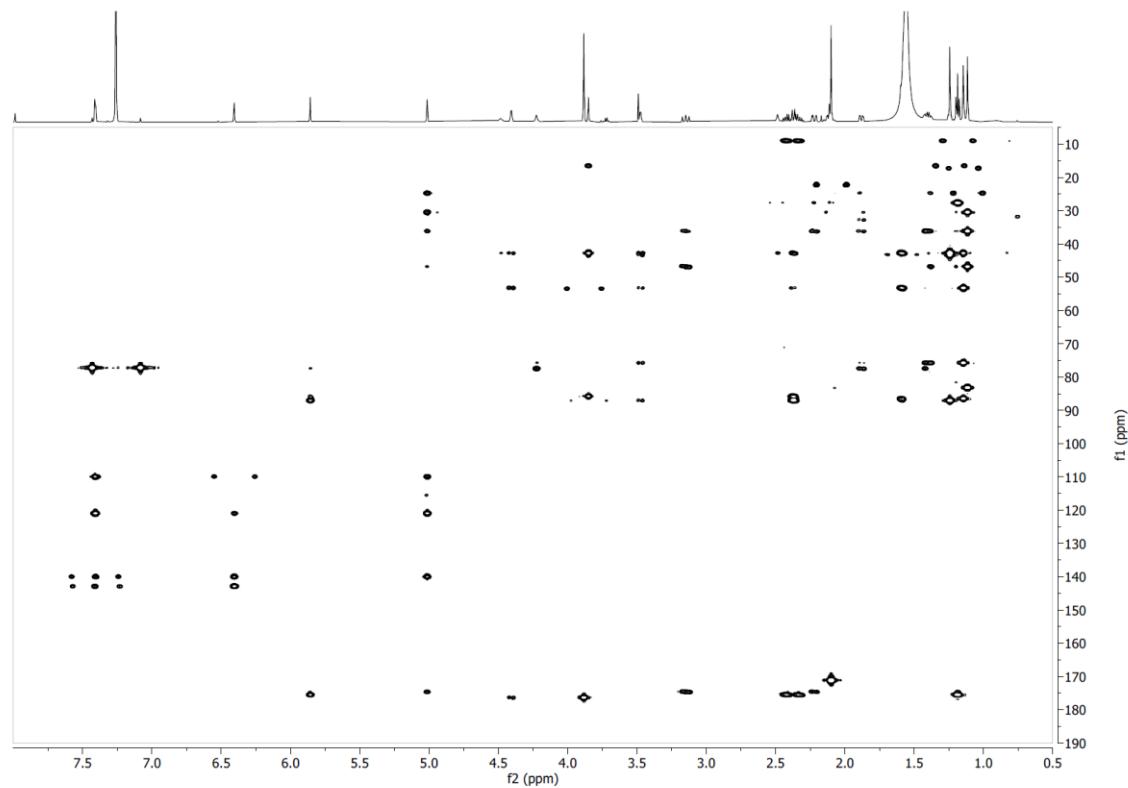
Supplementary Figure S4.2.9. ^1H NMR spectrum of compound **1** in CDCl_3 at 600 MHz



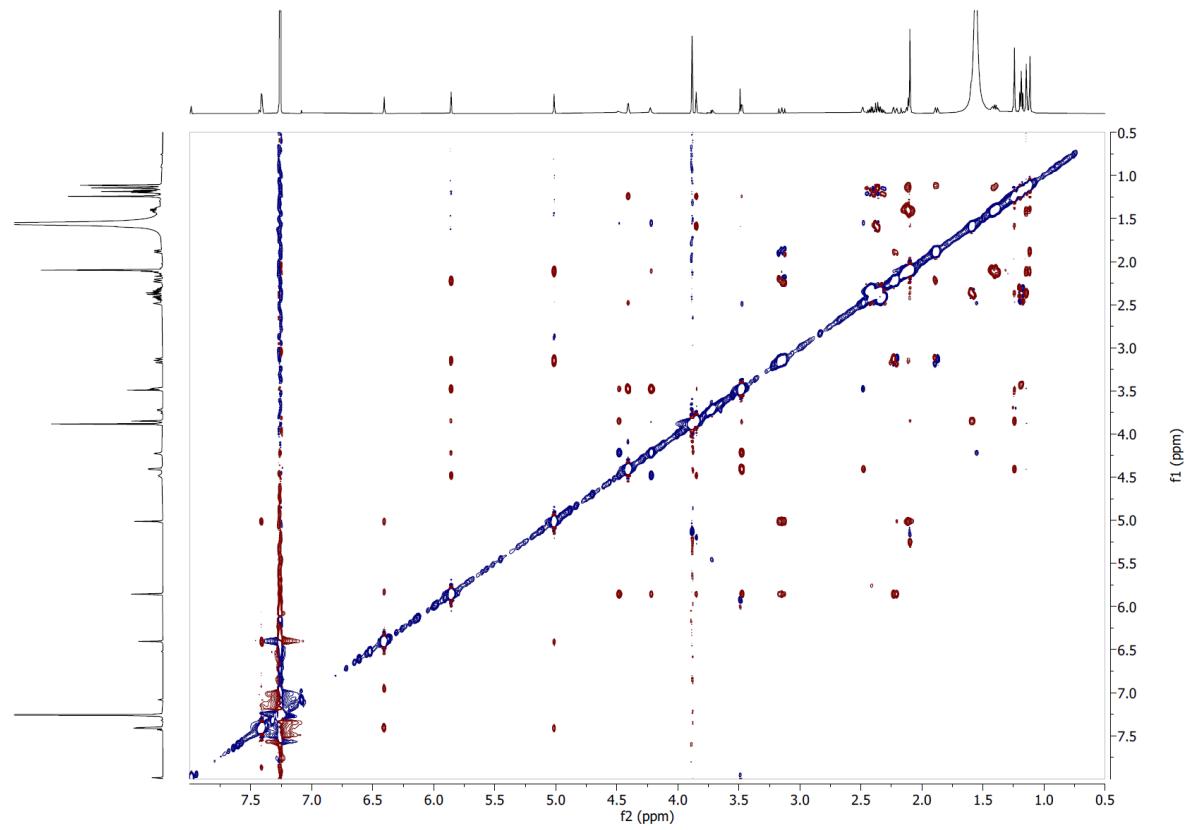
Supplementary Figure S4.2.10. COSY NMR spectrum of compound **1** in CDCl_3



Supplementary Figure S4.2.11. Edited HSQC NMR spectrum of compound **1** in CDCl_3

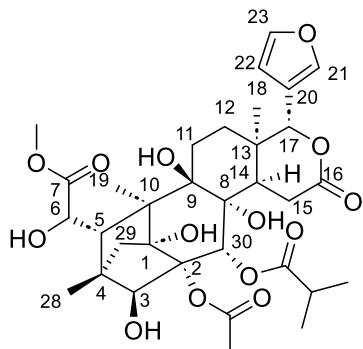


Supplementary Figure S4.2.12. HMBC NMR spectrum of compound **1** in CDCl_3



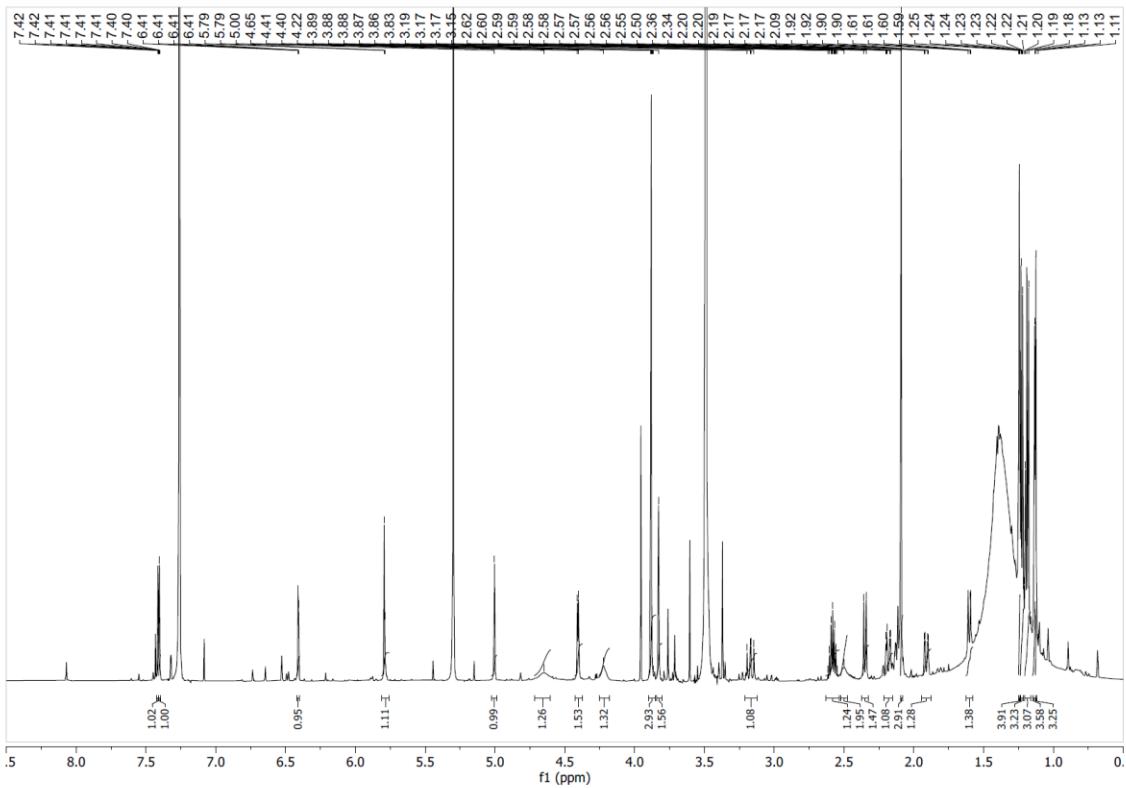
Supplementary Figure S4.2.13. ROESY NMR spectrum of compound **1** in CDCl_3

Compound 2. Amorphous white powder, HRESIMS m/z 687.2610 [M+Na]⁺ (calculated for C₃₃H₄₄O₁₄Na, error -0.97 ppm), 663.2657 [M-H]⁻ (calculated for C₃₃H₄₃O₁₄, error 1.53 ppm); $[\alpha]_D^{20}$ -0.8 (c 0.0004 CHCl₃); UV (c 0.0004, MeOH) λ_{max} 210, 251 nm.

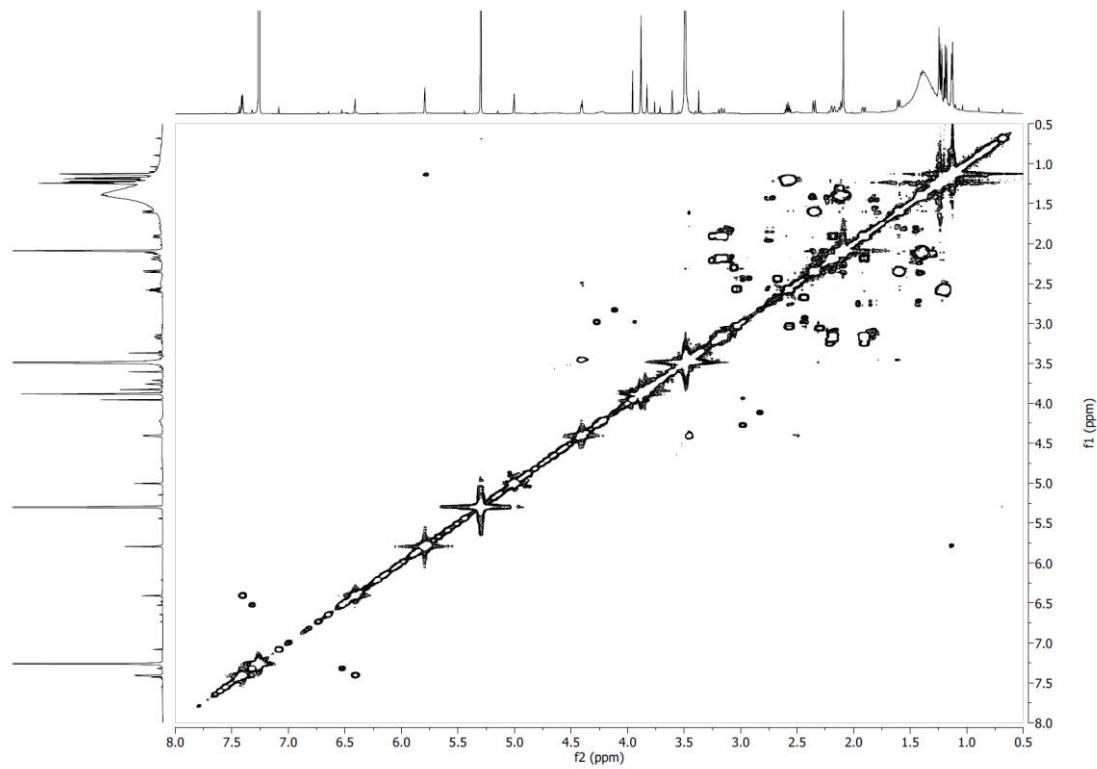


Chemical Formula: C₃₃H₄₄O₁₄
Exact Mass: 664.27

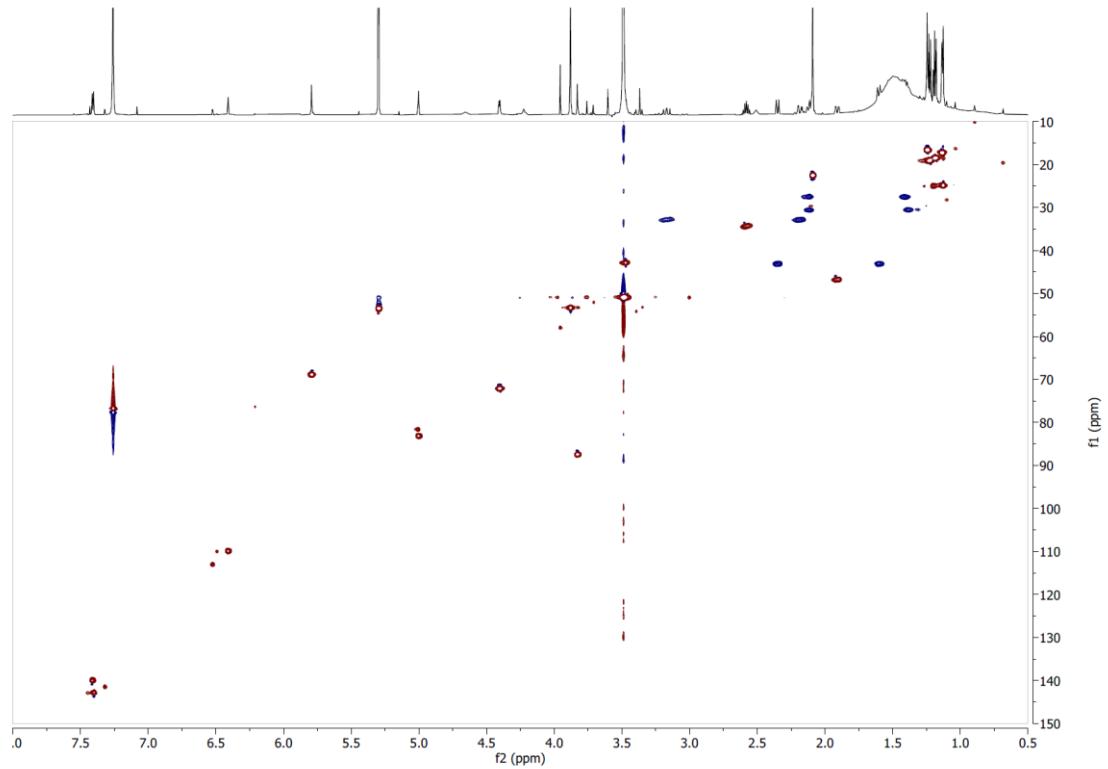
¹H NMR (CDCl₃, 600 MHz) δ 1.13 (3H, s, H₃-18), 1.13 (3H, s, H₃-19), 1.18 (3H, d, J = 7.1 Hz, H₃-30d), 1.23 (3H, d, J = 7.1 Hz, H₃-30c), 1.24 (3H, s, H₃-28), 1.39 (1H, overlapped, H-12a), 1.41 (1H, overlapped, H-11a), 1.60 (1H, d, J = 10.8 Hz, H-29proR), 1.91 (1H, dd, J = 13.1, 3.6 Hz, H-14), 2.09 (3H, s, H₃-2b), 2.11 (1H, overlapped, H-12b), 2.12 (1H, overlapped, H-11b), 2.18 (1H, dd, J = 15.7, 3.6 Hz, H-15α), 2.35 (1H, d, J = 10.8 Hz, H-29 proS), 2.50 (1H, s, OH-6), 2.58 (1H, hept, J = 7.1 Hz, H-30b), 3.17 (1H, dd, J = 15.7, 13.1 Hz, H-15β), 3.47 (1H, overlapped, H-5), 3.83 (1H, s, H-3), 3.88 (3H, s, OCH₃), 4.22 (1H, s, OH-9), 4.41 (2H, d, J = 4.4 Hz, H-6), 4.65 (1H, s, OH-3), 5.00 (1H, s, H-17), 5.79 (1H, s, H-30), 6.41 (1H, d, J = 1.7 Hz, H-22), 7.40 (1H, t, J = 1.7 Hz, H-23), 7.41 (1H, d, J = 1.7 Hz, H-21); ¹H NMR (CDCl₃, 151 MHz) δ 17.2 (CH₃-19), 18.4 (CH₃-30d), 19.1 (CH₃-28, CH₃-30c), 22.5 (CH₃-2b), 24.8 (CH₃-18), 27.5 (CH₂-11), 30.6 (CH₂-12), 32.9 (CH₂-15), 34.3 (CH-30b), 36.0 (C-13), 42.9 (CH-5), 43.0 (CH₂-29), 46.7 (CH-14), 53.3 (C-10), 53.4 (OCH₃), 68.9 (CH-30), 72.1 (CH-6), 75.8 (C-9), 77.3 (C-8), 83.1 (CH-17), 85.9 (C-2), 86.8 (C-1), 87.5 (CH-3), 109.9 (CH-22), 120.9 (C-20), 139.9 (CH-21), 142.8 (CH-23), 171.3 (C-2a), 174.4 (C-16), 176.4 (C-7), 178.2 (C-30a). **Supplementary Figures S4.2.14–S4.2.18.**



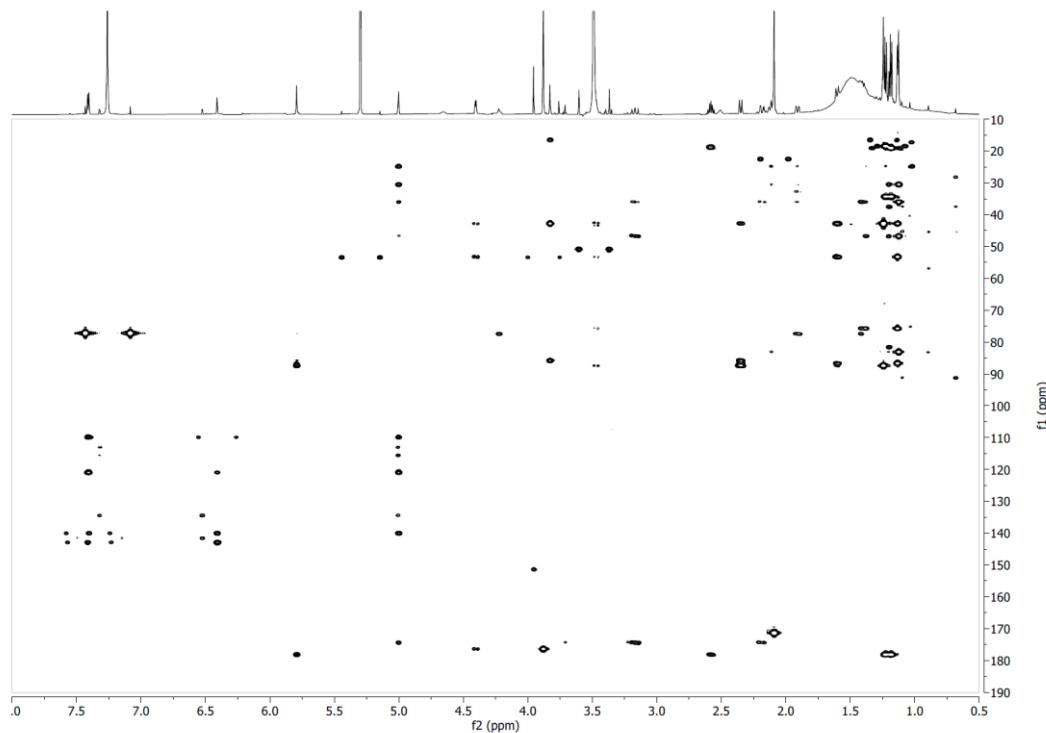
Supplementary Figure S4.2.14. ^1H NMR spectrum of compound **2** in CDCl_3 at 600 MHz



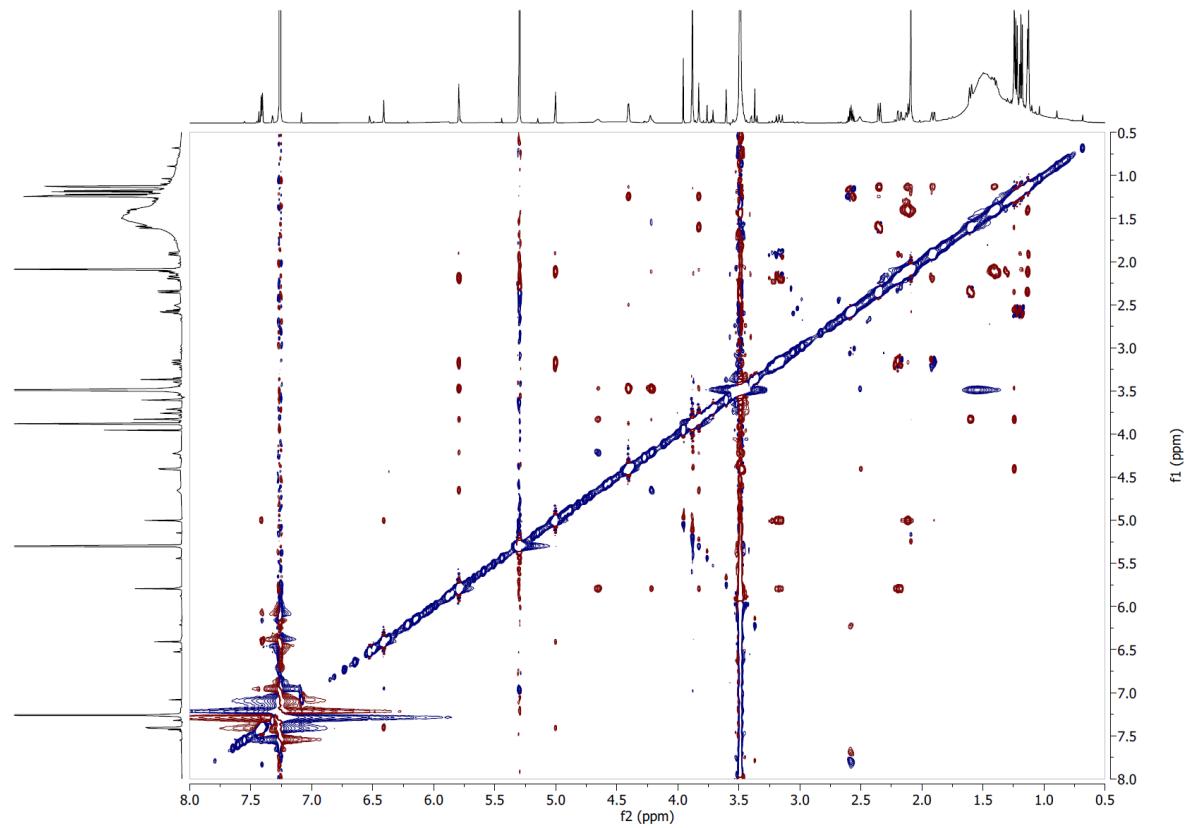
Supplementary Figure S4.2.15. COSY NMR spectrum of compound **2** in CDCl_3



Supplementary Figure S4.2.16. Edited HSQC NMR spectrum of compound **2** in CDCl_3

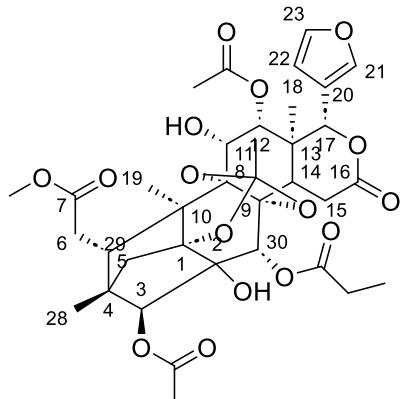


Supplementary Figure S4.2.17. HMBC NMR spectrum of compound **2** in CDCl_3



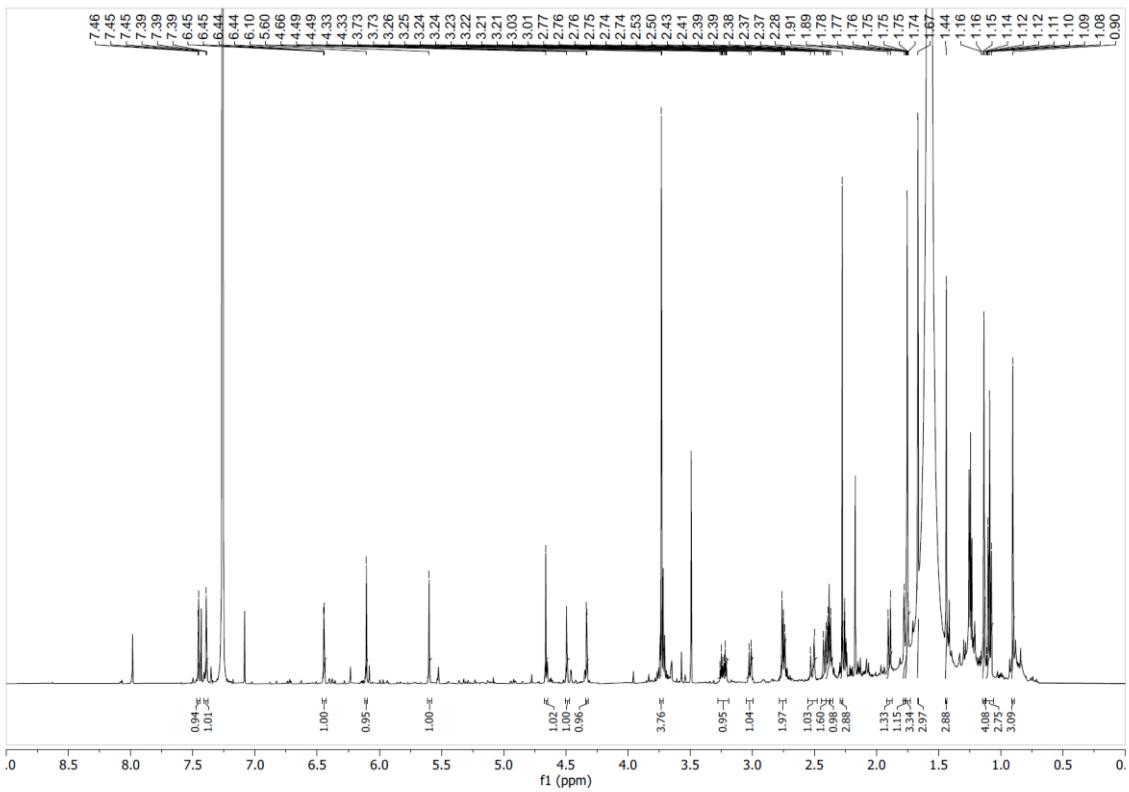
Supplementary Figure S4.2.18. ROESY NMR spectrum of compound **2** in CDCl_3

Compound 3: Carapanolide M [57]. Amorphous white powder, HRESIMS m/z 733.2702 [$M+H$]⁺ (calculated for C₃₆H₄₅O₁₆, error -0.01 ppm), 731.2524 [$M-H$]⁻ (calculated for C₃₆H₄₃O₁₆, error -2.90 ppm); $[\alpha]_D^{20}$ -59 (c 0.0002 CHCl₃); UV (c 0.002, MeOH) λ_{max} 200, 225 nm (s).

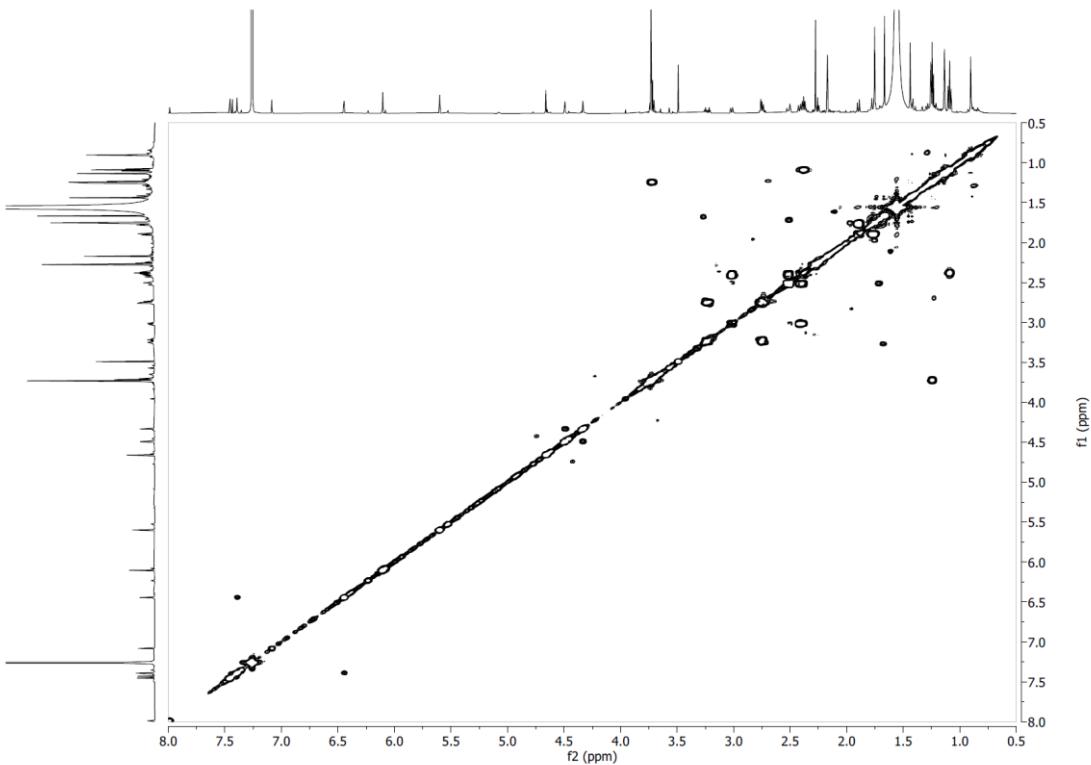


Chemical Formula: C₃₆H₄₄O₁₆
Exact Mass: 732.26

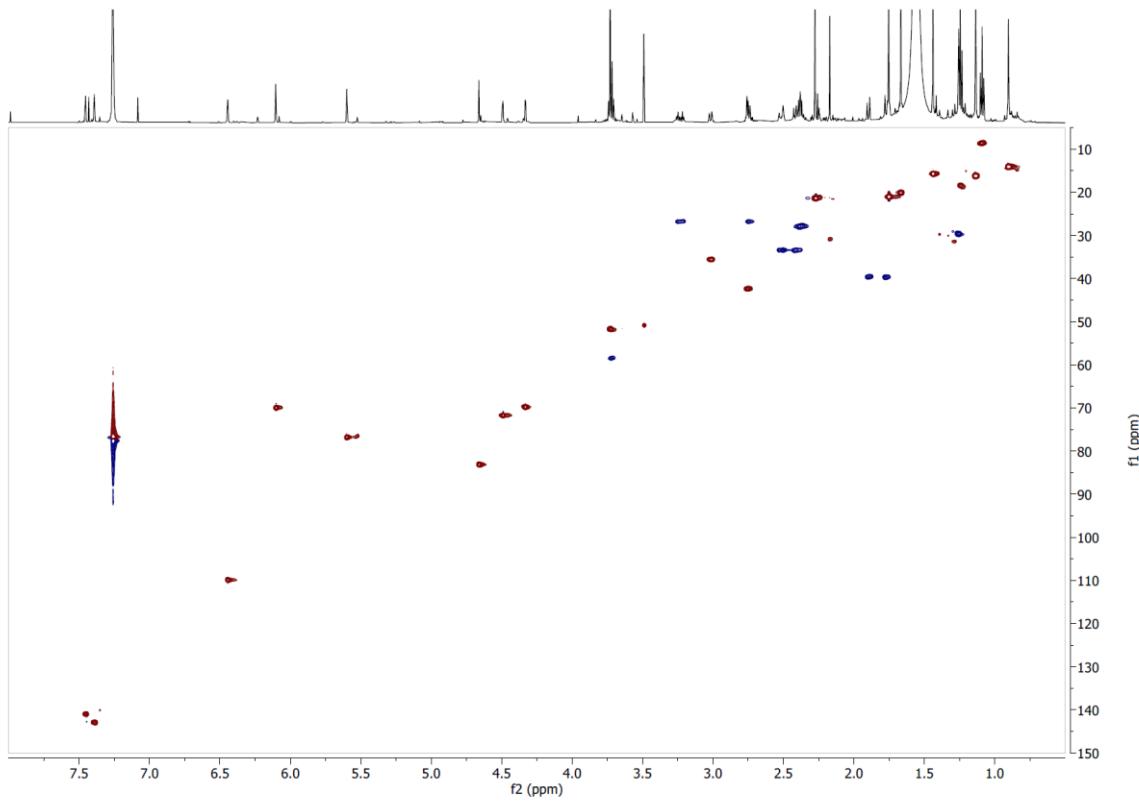
¹H NMR (CDCl₃, 600 MHz) δ 0.90 (3H, s, H₃-28), 1.09 (3H, t, J = 7.5 Hz, H₃-30c), 1.14 (3H, s, H₃-19), 1.44 (3H, s, H₃-18), 1.67 (3H, s, H₃-12b), 1.75 (3H, s, H₃-34), 1.77 (1H, d, J = 10.8 Hz, H-29''), 1.90 (1H, d, J = 10.8 Hz, H-29'), 2.28 (3H, s, H₃-3b), 2.38 (1H, m, H-30b', H-30b''), 2.40 (1H, dd, J = 17.3, 10.4 Hz, H-6''), 2.52 (1H, d, J = 17.3 Hz, H-6'), 2.75 (2H, m, H-14, H-15b), 3.02 (1H, d, J = 10.4 Hz, H-5), 3.23 (1H, dt, J = 18.5, 5.8 Hz, H-15a), 3.73 (3H, s, OCH₃), 4.33 (1H, d, J = 2.3 Hz, H-11), 4.49 (1H, d, J = 2.3 Hz, H-12), 4.66 (1H, s, H-3), 5.60 (1H, s, H-17), 6.10 (1H, s, H-30), 6.44 (1H, t, J = 1.7 Hz, H-22), 7.39 (1H, t, J = 1.7 Hz, H-23), 7.45 (1H, t, J = 1.7 Hz, H-21); ¹³C NMR (CDCl₃, 151 MHz) δ 8.5 (CH₃-30c), 14.0 (CH₃-28), 15.7 (CH₃-18), 16.3 (CH₃-19), 20.1 (CH₃-12b), 21.0 (CH₃-34), 21.4 (CH₃-3b), 26.8 (CH₂-15), 27.9 (CH₂-30b), 33.3 (CH₂-6), 35.6 (CH-5), 38.5 (C-13), 39.5 (CH₂-29), 42.3 (CH-14), 45.1 (C-10), 45.4 (C-4), 51.8 (OCH₃), 69.7 (CH-11), 69.9 (CH-30), 71.7 (CH-12), 76.8 (CH-17), 79.6 (C-2), 83.1 (CH-3), 85.2 (C-1), 85.7 (C-9), 86.1 (C-8), 109.8 (CH-22), 119.4 (C-33), 129.9 (C-20), 140.9 (CH-21), 142.9 (CH-23), 169.7 (C-12a), 169.9 (C-16), 171.0 (C-3a), 172.2 (C-7), 172.4 (C-30a). **Supplementary Figures S4.2.19-S4.2.23.**



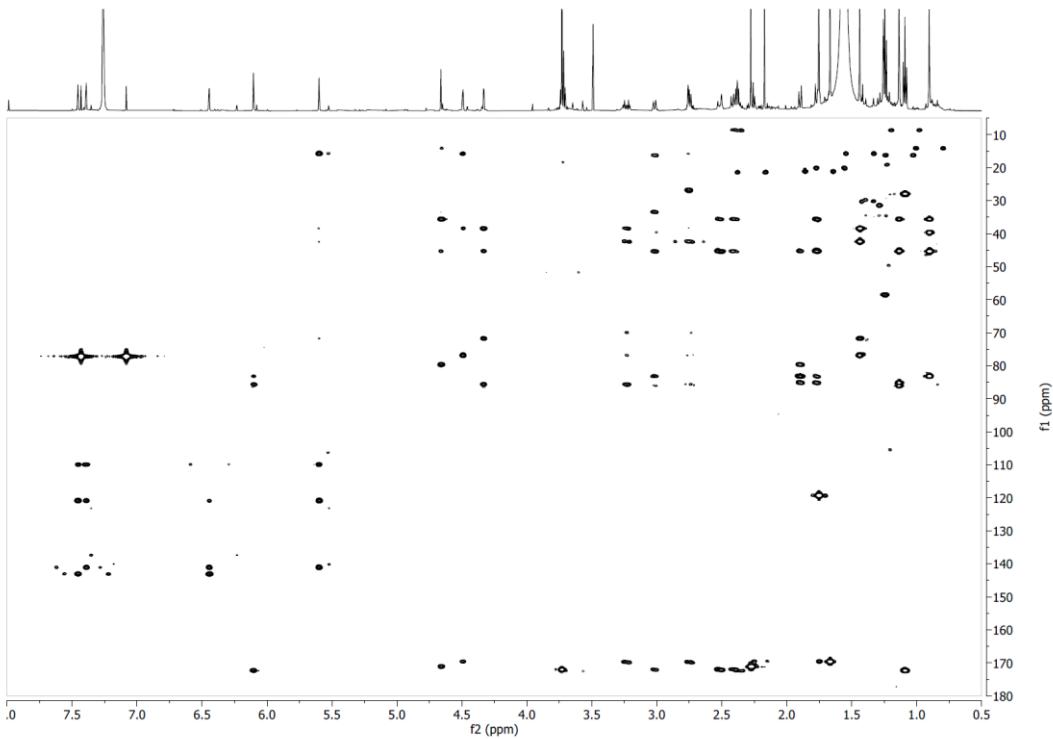
Supplementary Figure S4.2.19. ^1H NMR spectrum of compound **3** in CDCl_3 at 600 MHz



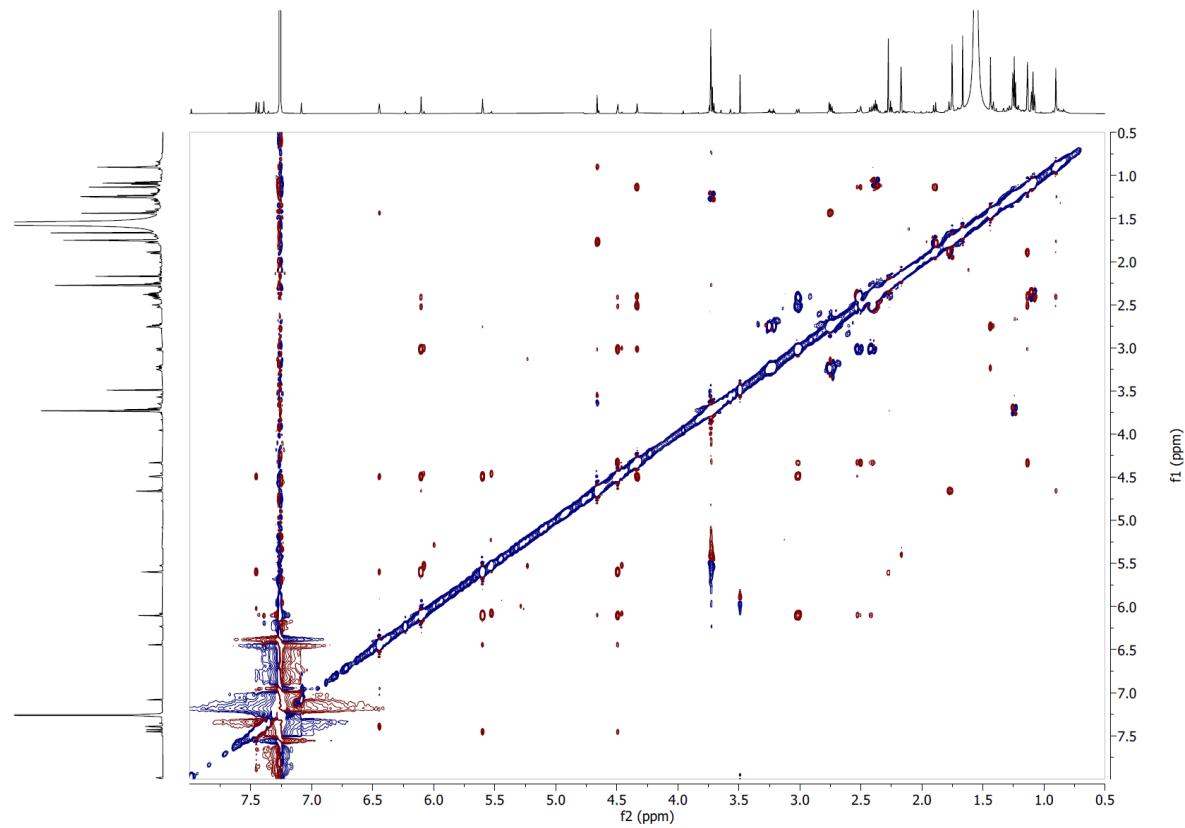
Supplementary Figure S4.2.20. COSY NMR spectrum of compound **3** in CDCl_3



Supplementary Figure S4.2.21. Edited HSQC NMR spectrum of compound **3** in CDCl_3

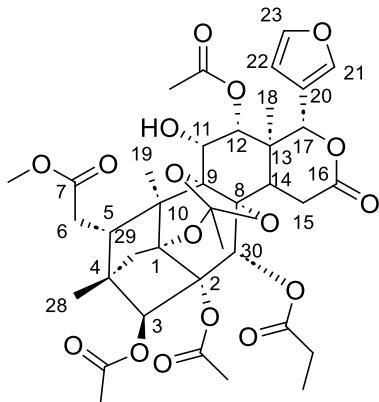


Supplementary Figure S4.2.22. HMBC NMR spectrum of compound **3** in CDCl_3



Supplementary Figure S4.2.23. ROESY NMR spectrum of compound **3** in CDCl_3

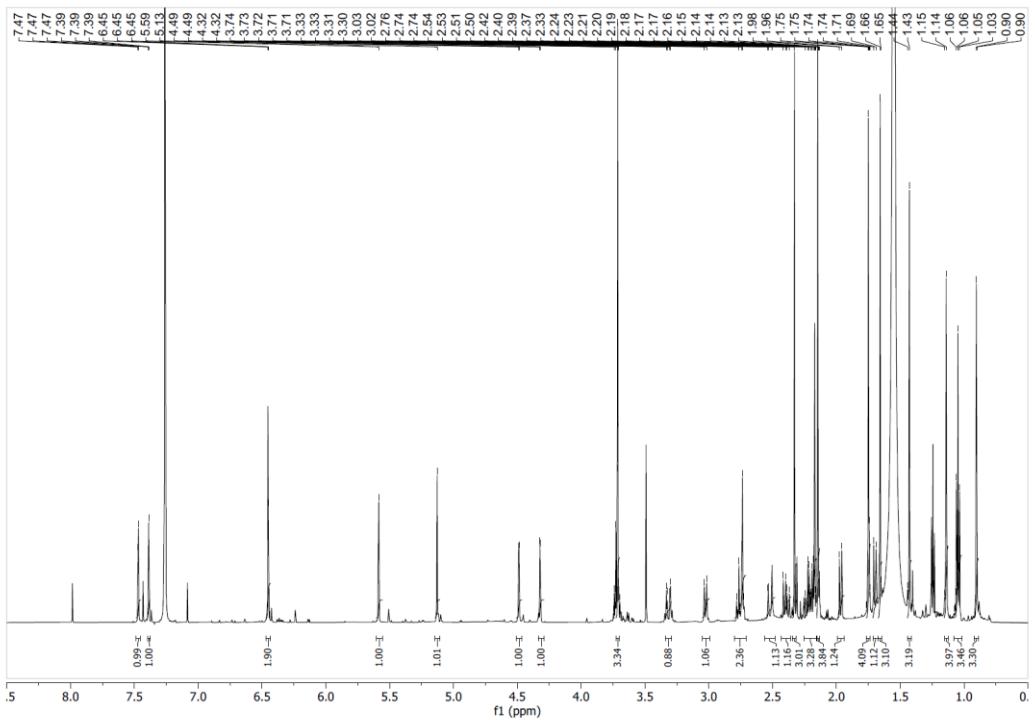
Compound 4. Amorphous white powder, HRESIMS m/z 775.2807 [M+H]⁺ (calculated for C₃₈H₄₇O₁₇Na, error -0.02 ppm), 773.2686 [M-H]⁻ (calculated for C₃₈H₄₅O₁₇, error 4.59 ppm); $[\alpha]_D^{20} -44$ (c 0.0005 CHCl₃); UV (c 0.005, MeOH) λ_{max} 193, 220 nm (s).



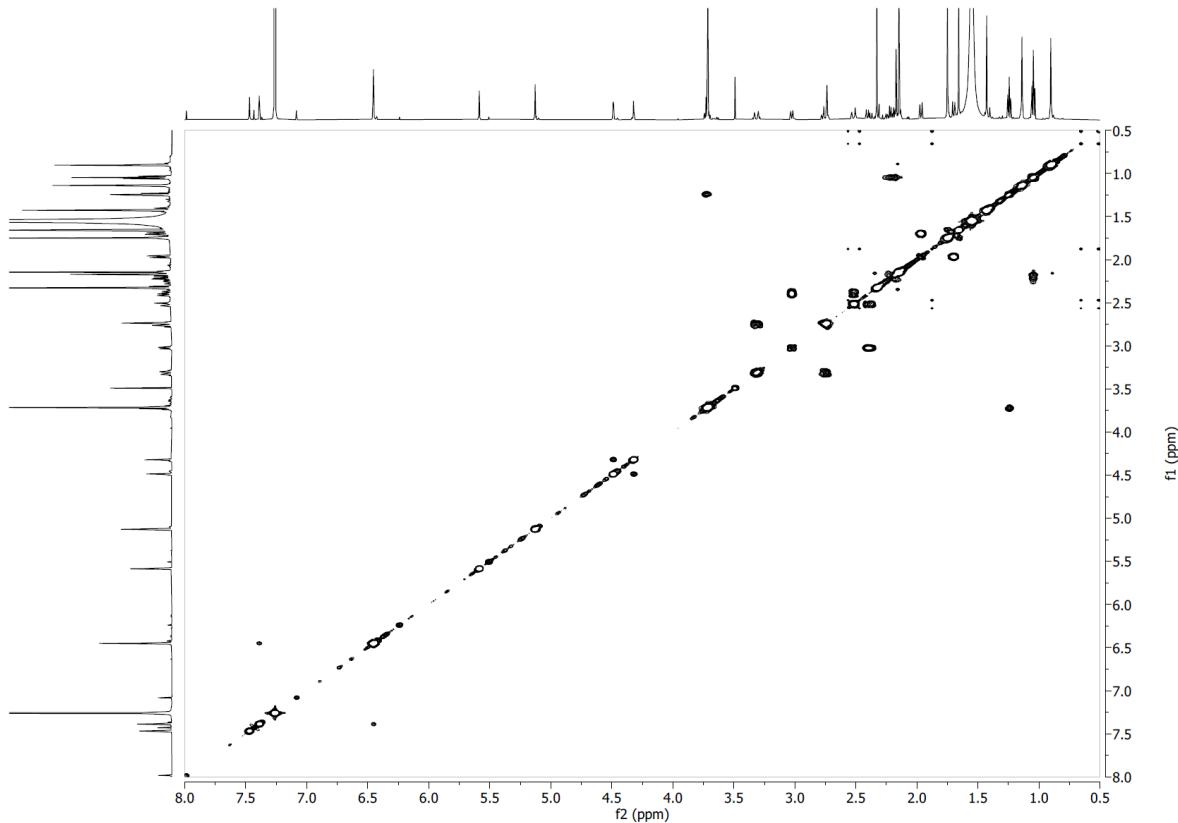
Chemical Formula: C₃₈H₄₆O₁₇

Exact Mass: 774.27

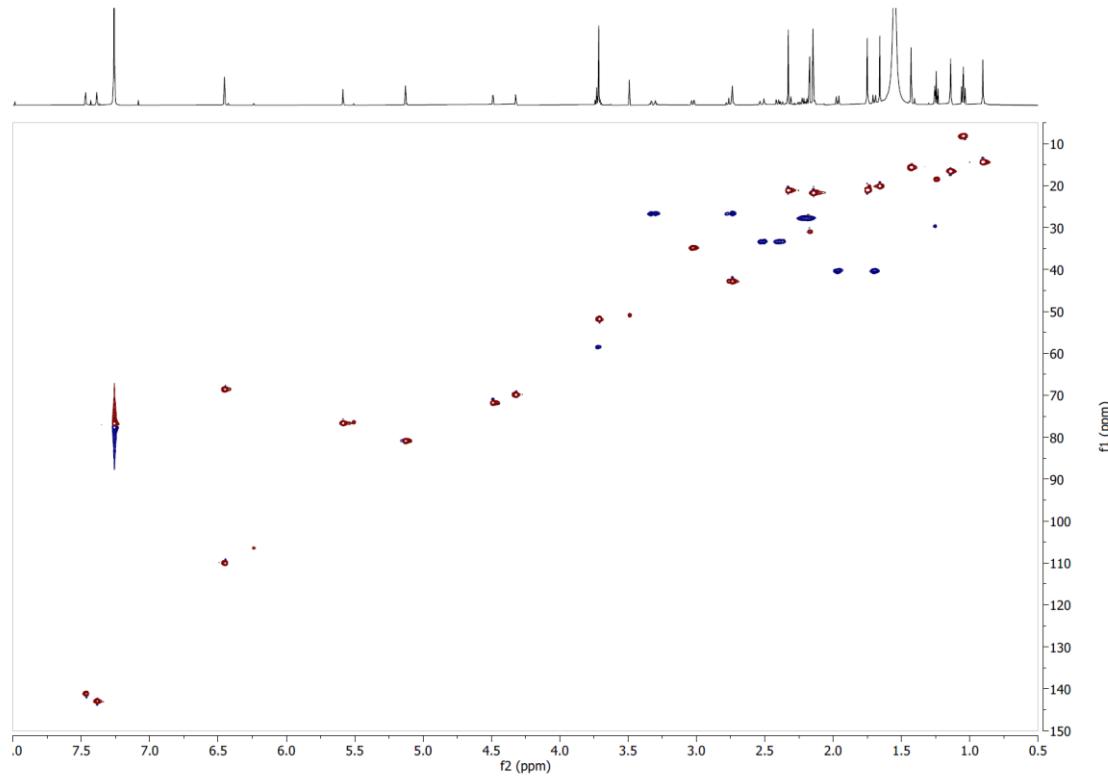
¹H NMR (CDCl₃, 600 MHz) δ 0.90 (3H, s, H₃-28), 1.05 (3H, t, J = 7.4 Hz, H₃-30c), 1.14 (3H, s, H₃-19), 1.43 (3H, s, H₃-18), 1.66 (3H, s, H₃-12b), 1.70 (1H, d, J = 11.1 Hz, H-29¹¹), 1.75 (3H, d, J = 4.5 Hz, H₃-34), 1.97 (1H, d, J = 11.1 Hz, H-29¹), 2.15 (3H, s, H₃-2b), 2.20 (2H, m, H-30b¹, H-30b¹¹), 2.33 (3H, s, H₃-3b), 2.39 (1H, dd, J = 17.6, 10.7 Hz, H-6¹¹), 2.52 (1H, dd, J = 17.6, 1.6 Hz, H-6¹), 2.76 (2H, m, H-14, H-15 β), 3.03 (1H, d, J = 10.7 Hz, H-5), 3.32 (1H, dd, J = 16.0, 3.3 Hz, H-15 α), 3.71 (3H, s, OCH₃), 4.32 (1H, d, J = 2.2 Hz, H-11), 4.49 (1H, d, J = 2.2 Hz, H-12), 5.13 (1H, s, H-3), 5.59 (1H, s, H-17), 6.45 (2H, m, H-22, H-30), 7.39 (1H, t, J = 1.5 Hz, H-23), 7.47 (1H, t, J = 1.5 Hz, H-21); ¹³C NMR (CDCl₃, 151 MHz) δ 8.2 (CH₃-30c), 14.4 (CH₃-28), 15.6 (CH₃-18), 16.5 (CH₃-19), 20.0 (CH₃-12b), 21.1 (CH₃-3b, CH₃-34), 21.8 (CH₃-2b), 26.7 (CH₂-15), 27.8 (CH₂-30b), 33.3 (CH₂-6), 34.8 (CH-5), 38.5 (C-13), 40.3 (CH₂-29), 42.9 (CH-14), 45.9 (C-10), 46.1 (C-4), 51.8 (OCH₃), 68.5 (CH-30), 70.0 (CH-11), 71.7 (CH-12), 76.6 (CH-17), 80.9 (CH-3), 84.7 (C-8), 85.0 (C-1), 85.7 (C-2), 85.9 (C-9), 110.0 (CH-22), 119.4 (C-33), 120.9 (C-20), 141.2 (CH-21), 142.9 (CH-23), 169.6 (C-12a), 169.8 (C-16), 170.1 (C-2a), 170.4 (C-3a), 171.7 (C-30a), 171.9 (C-7). **Supplementary Figures S4.2.24-S4.2.28.**



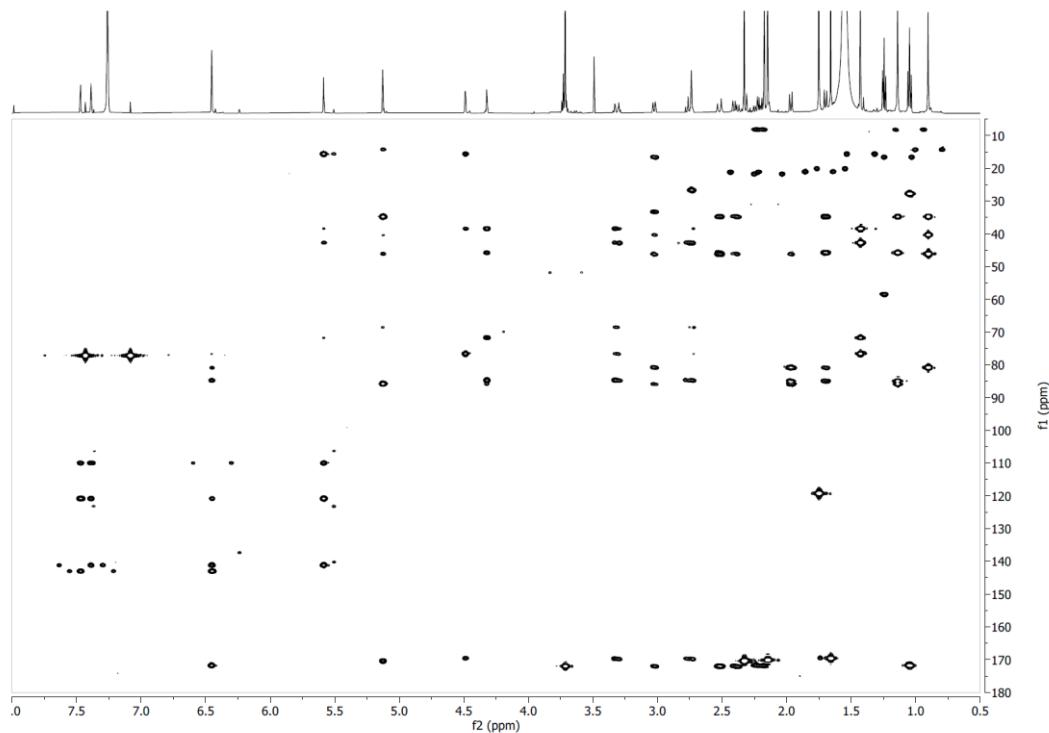
Supplementary Figure S4.2.24. ^1H NMR spectrum of compound 4 in CDCl_3 at 600 MHz



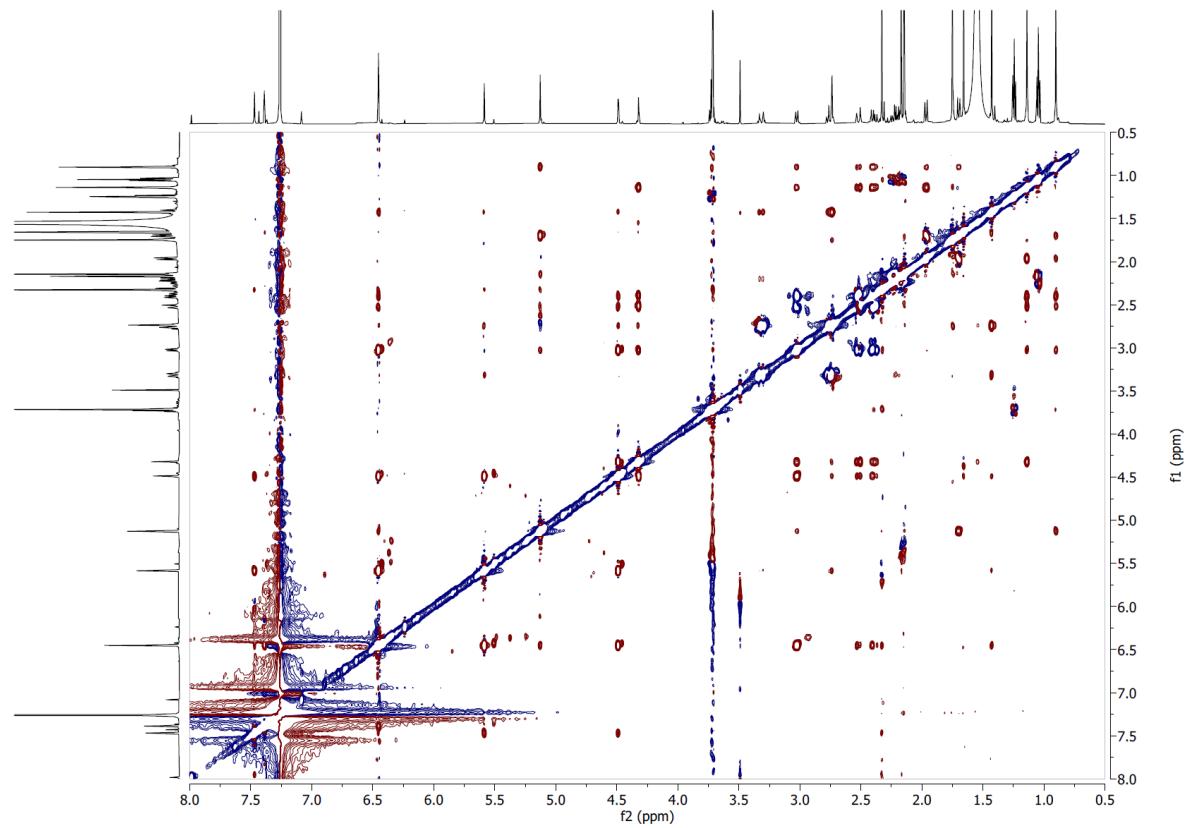
Supplementary Figure S4.2.25. COSY NMR spectrum of compound 4 in CDCl_3



Supplementary Figure S4.2.26. Edited HSQC NMR spectrum of compound **4** in CDCl_3

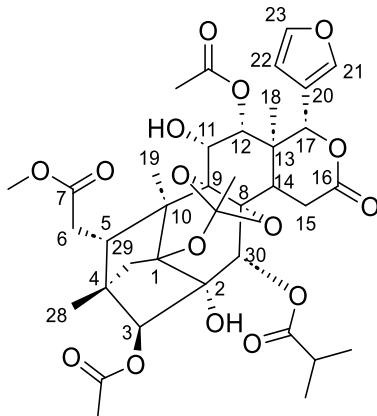


Supplementary Figure S4.2.27. HMBC NMR spectrum of compound **4** in CDCl_3



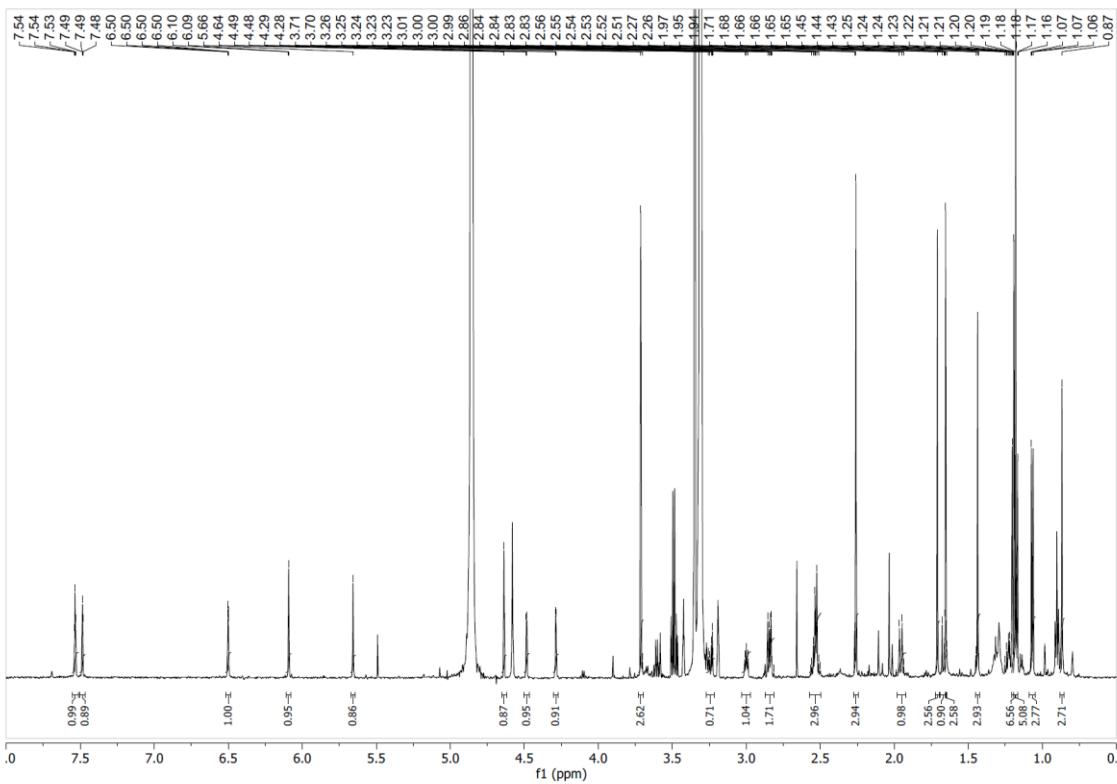
Supplementary Figure S4.2.28. ROESY NMR spectrum of compound **4** in CDCl_3

Compound 5: Guianfruit H [58]. Amorphous white powder, HRESIMS m/z 747.2861 [$M+H$]⁺ (calculated for C₃₇H₄₇O₁₆, error 0.35 ppm), 745.2717 [$M-H$]⁻ (calculated for C₃₇H₄₅O₁₆, error 2.03 ppm); $[\alpha]_D^{20} -33$ (c 0.0002 CHCl₃); UV (c 0.002, MeOH) λ_{max} 203 nm.

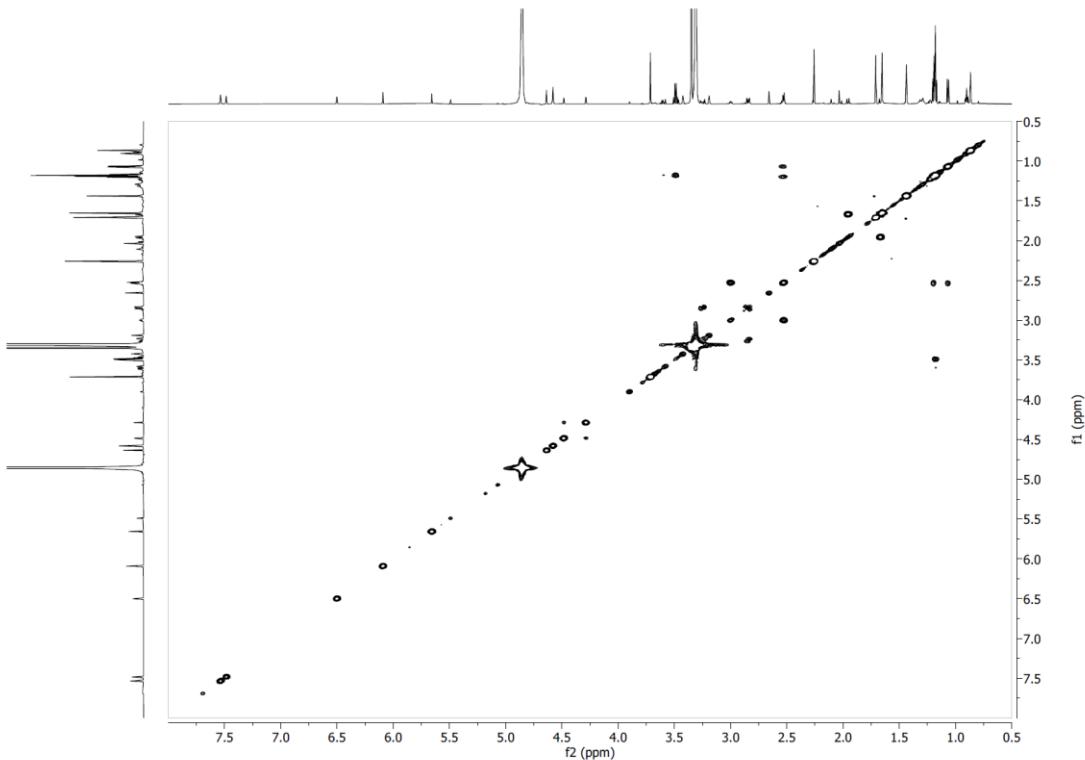


Chemical Formula: C₃₇H₄₆O₁₆
Exact Mass: 746.28

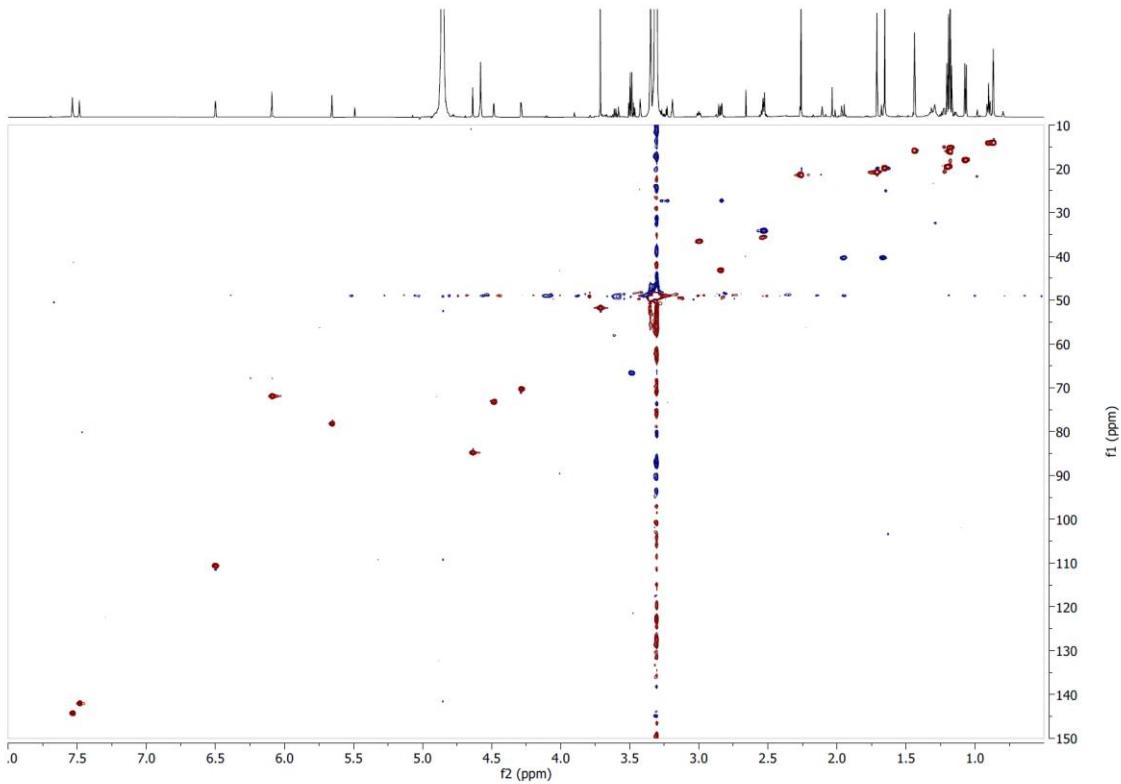
¹H NMR (CD₃OD, 600 MHz) δ 0.87 (3H, s, H₃-28), 1.07 (3H, d, J = 6.8 Hz, H₃-30d), 1.18 (3H, s, H₃-19), 1.19 (3H, d, J = 6.8 Hz, H₃-30c), 1.44 (3H, s, H₃-18), 1.65 (3H, s, H₃-12b), 1.67 (1H, d, J = 10.7 Hz, H-29''), 1.71 (3H, s, H₃-34), 1.96 (1H, d, J = 10.7 Hz, H-29'), 2.26 (3H, s, H₃-3b), 2.53 (3H, m, H₂-6, H-30b), 2.84 (2H, m, H-14, H-15''), 3.00 (1H, dd, J = 7.2, 5.6 Hz, H-5), 3.24 (1H, dd, J = 11.7, 4.5 Hz, H-15'), 3.71 (3H, s, OCH₃), 4.29 (1H, d, J = 2.4 Hz, H-11), 4.48 (1H, d, J = 2.4 Hz, H-12), 4.64 (1H, s, H-3), 5.66 (1H, s, H-17), 6.09 (1H, s, H-30), 6.50 (1H, t, J = 1.8 Hz, H-22), 7.49 (1H, t, J = 1.8 Hz, H-21), 7.54 (1H, t, J = 1.8 Hz, H-23); ¹³C NMR (CD₃OD, 151 MHz) δ 14.1 (CH₃-28), 15.8 (CH₃-18), 16.0 (CH₃-19), 17.9 (CH₃-30d), 19.5 (CH₃-30c), 19.9 (CH₃-12b), 20.7 (CH₃-34), 21.4 (CH₃-3b), 27.3 (CH₂-15), 34.1 (CH₂-6), 35.7 (CH-30b), 36.6 (CH-5), 39.3 (C-13), 40.3 (CH₂-29), 43.1 (CH-14), 46.0 (C-10), 46.2 (C-4), 51.7 (OCH₃), 70.3 (CH-11), 71.9 (CH-30), 73.1 (CH-12), 78.1 (CH-17), 80.8 (C-2), 84.8 (CH-3), 86.0 (C-1), 86.2 (C-8), 87.6 (C-9), 110.6 (CH-22), 120.4 (C-33), 122.2 (C-20), 142.1 (CH-21), 144.4 (CH-23), 170.7 (C-12a), 172.3 (C-3a), 172.5 (C-16), 174.1 (C-7), 176.3 (C-30a). Supplementary Figures S4.2.29-S4.2.33.



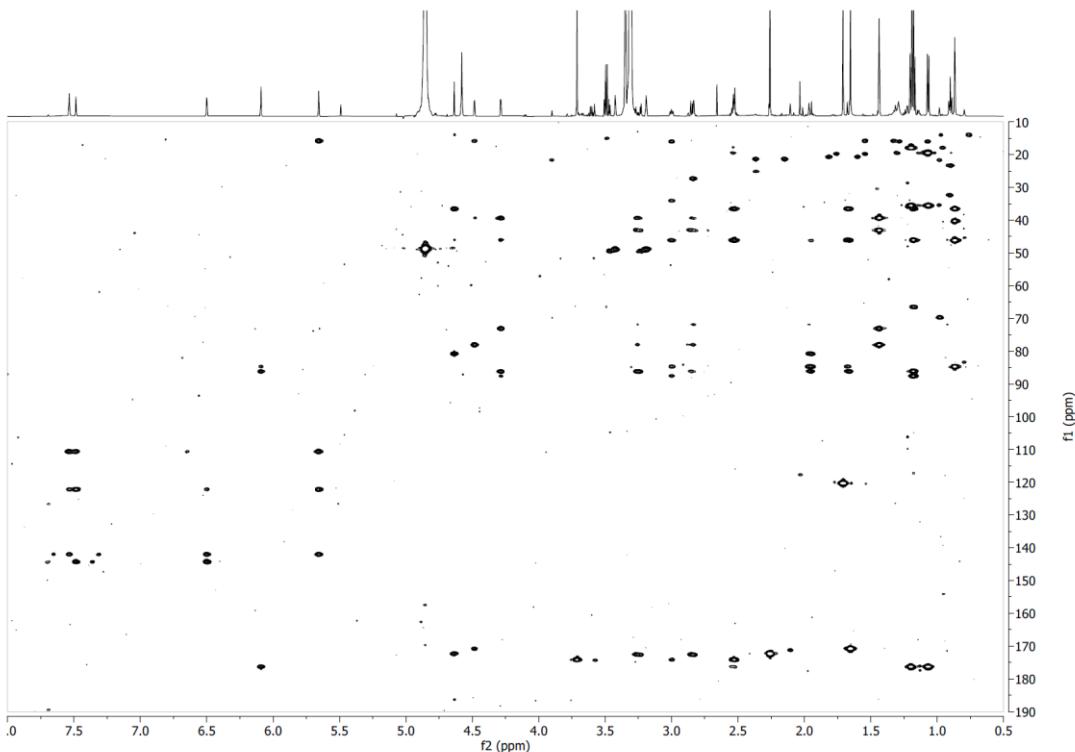
Supplementary Figure S4.2.29. ^1H NMR spectrum of compound 5 in CDCl_3 at 600 MHz



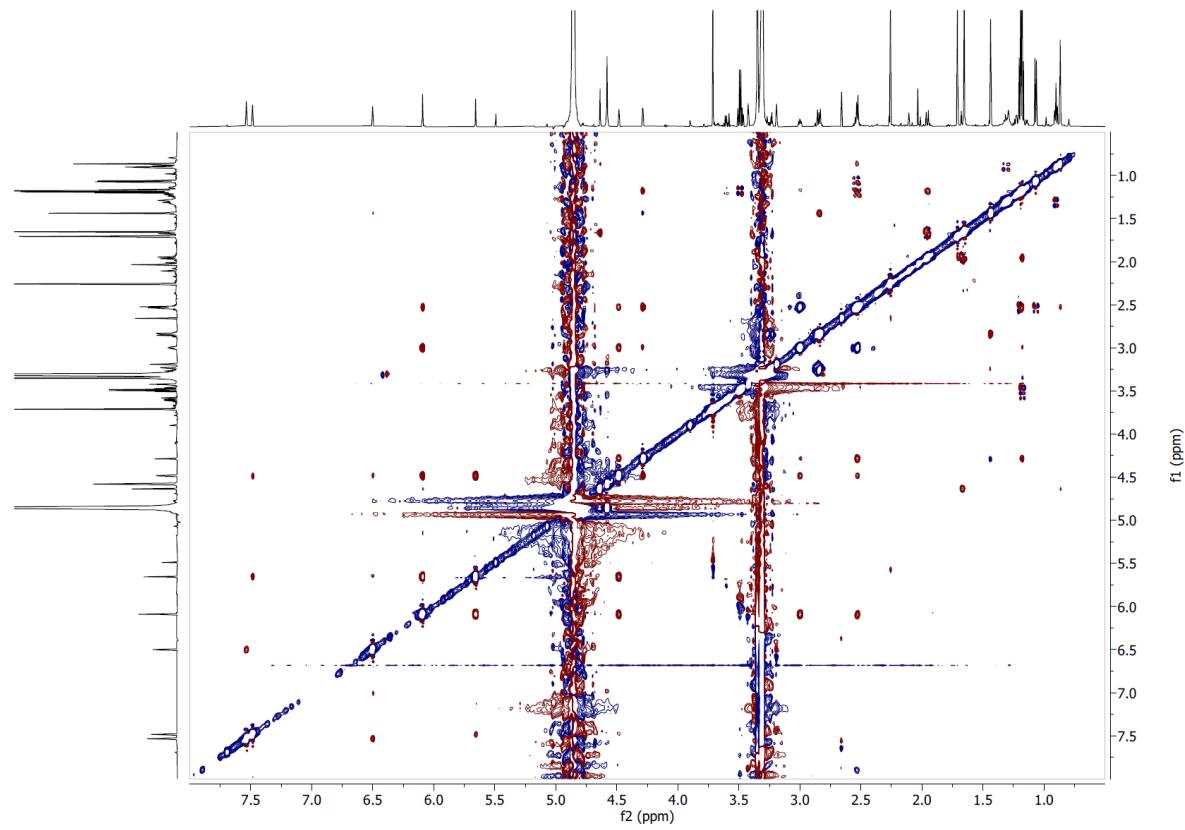
Supplementary Figure S4.2.30. COSY NMR spectrum of compound 5 in CDCl_3



Supplementary Figure S4.2.31. Edited HSQC NMR spectrum of compound 5 in CDCl_3

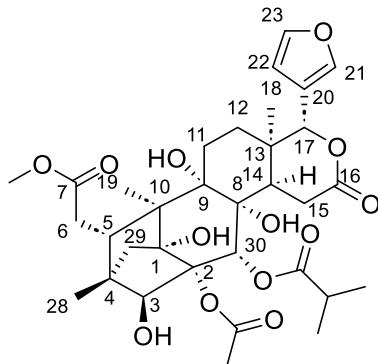


Supplementary Figure S4.2.32. HMBC NMR spectrum of compound 5 in CDCl_3



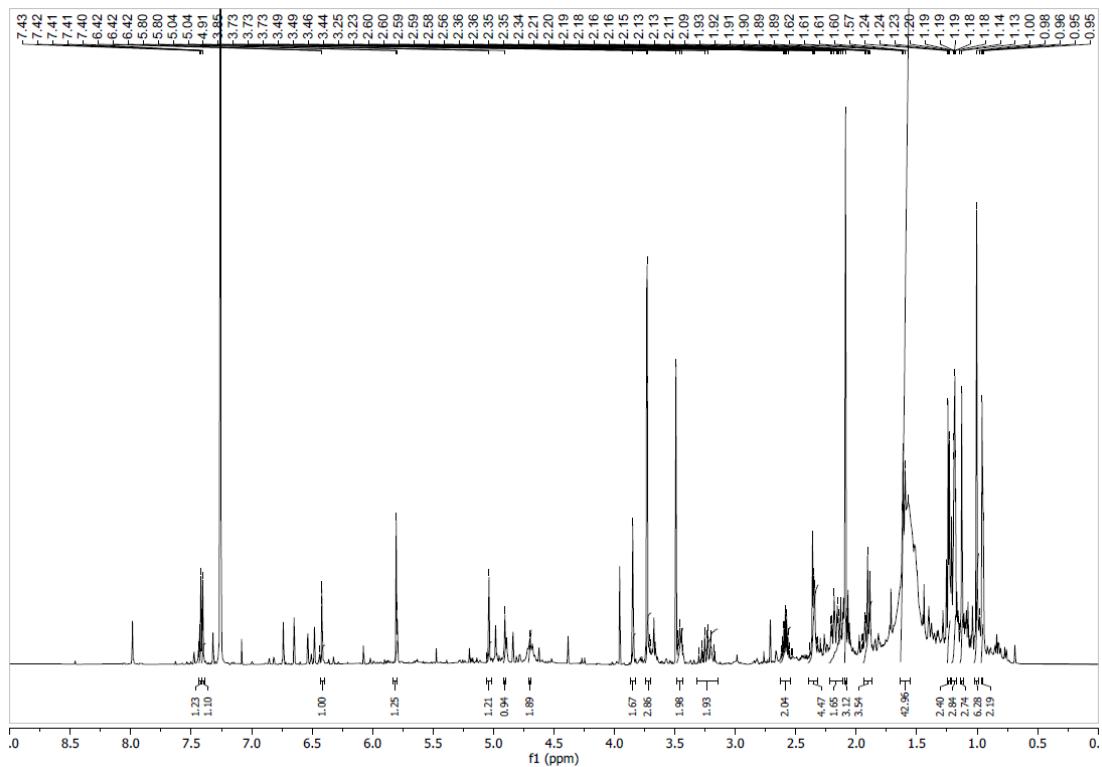
Supplementary Figure S4.2.33. ROESY NMR spectrum of compound **5** in CDCl_3

Compound 6. Amorphous white powder, HRESIMS m/z 671.2673 [M+Na]⁺ (calculated for C₃₃H₄₄O₁₃Na, error -0.12 ppm), 647.2706 [M-H]⁻ (calculated for C₃₃H₄₃O₁₃, error 1.25 ppm); $[\alpha]_D^{20}$ -15 (c 0.0009 CHCl₃); UV (c 0.0009, MeOH) λ_{max} λ_{max} 210, 251 nm.

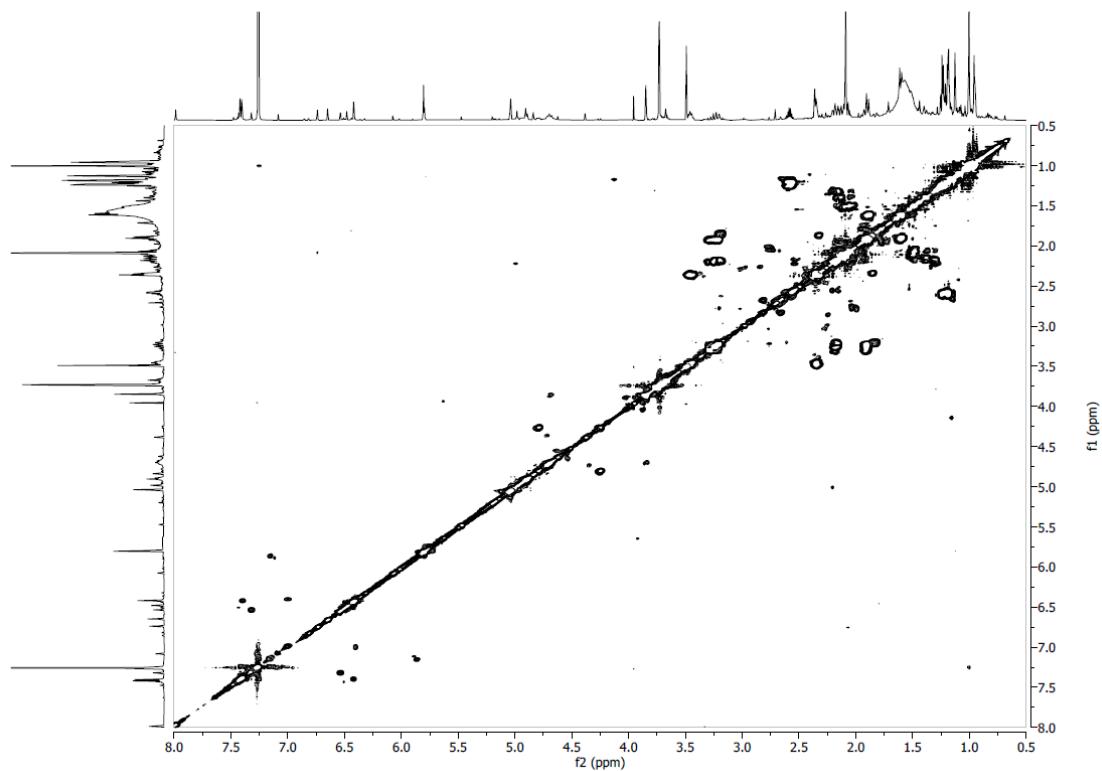


Chemical Formula: C₃₃H₄₄O₁₃
Exact Mass: 648.28

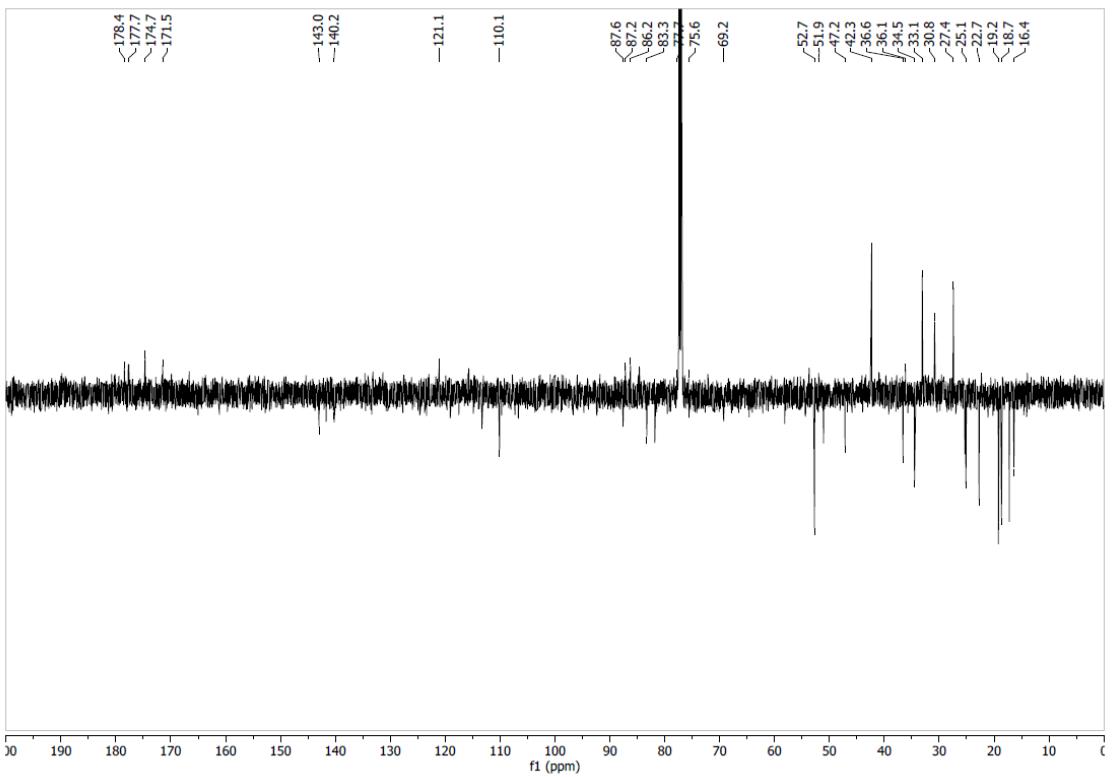
¹H NMR (CDCl₃, 600 MHz) δ 0.96 (3H, s, H₃-19), 1.00 (3H, s, H₃-28), 1.13 (3H, s, H₃-18), 1.19 (3H, d, J = 7.0 Hz, H₃-30d), 1.24 (3H, d, J = 7.0 Hz, H₃-30c), 1.37 (1H, m, H-12a), 1.50 (1H, m, H-11a), 1.60 (1H, m, H-29*pro-R*), 1.91 (2H, m, H-14, H-29 *pro-S*), 2.06 (1H, m, H-11b), 2.09 (3H, s, H₃-2b), 2.16 (1H, m, H-12b), 2.18 (1H, m, H-15a), 2.35 (2H, m, H₂-6), 2.59 (1H, hept, J = 7.0 Hz, H-30b), 3.22 (1H, m, H-15b), 3.46 (1H, m, H-5), 3.73 (3H, s, OCH₃), 3.85 (1H, s, H-3), 4.70 (2H, brs, 1-OH, 3-OH), 4.91 (1H, s, 9-OH), 5.04 (1H, s, H-17), 5.80 (1H, s, H-30), 6.42 (1H, d, J = 1.7 Hz, H-22), 7.41 (1H, d, J = 1.7 Hz, H-23), 7.42 (1H, s, H-21); ¹³C NMR (CDCl₃, 151 MHz) δ 16.4 (CH₃-19), 18.7 (CH₃-30d), 19.2 (CH₃-30c), 22.7 (CH₃-2b), 25.1 (CH₃-18), 27.4 (CH₂-11), 30.8 (CH₂-12), 33.1 (CH₂-6, CH₂-15), 34.5 (CH₃-30b), 36.1 (C-13), 36.6 (CH-5), 42.3 (CH₂-29), 47.2 (CH-14), 51.9 (C-10), 52.7 (OCH₃), 69.2 (CH-30), 75.6 (C-9), 77.7 (C-8), 83.3 (CH-17), 86.2 (C-2), 87.2 (C-1), 87.6 (CH-3), 110.1 (CH-22), 121.1 (C-20), 140.2 (CH-21), 143.0 (CH-23), 171.5 (C-2a), 174.7 (C-16), 177.7 (C-7), 178.4 (C-30a). Supplementary Figures S4.2.34-S4.2.39.



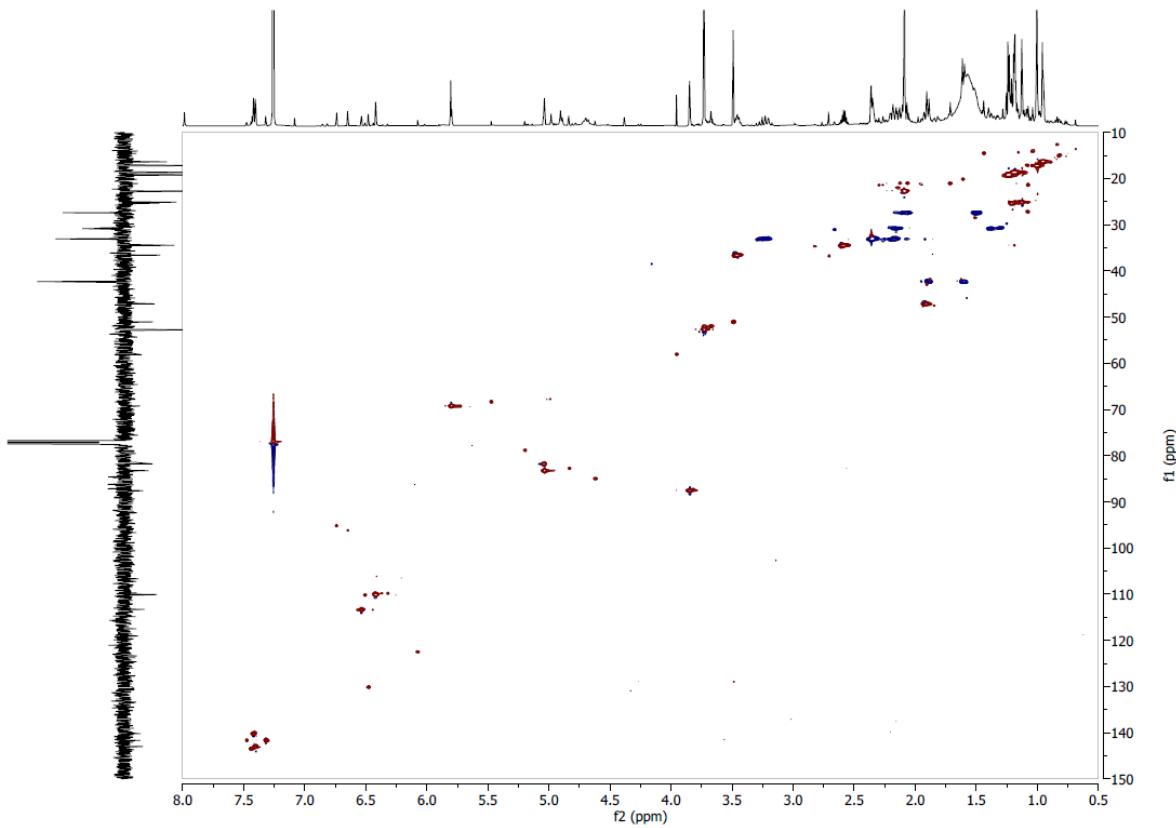
Supplementary Figure S4.2.34. ^1H NMR spectrum of compound **6** in CDCl_3 at 600 MHz



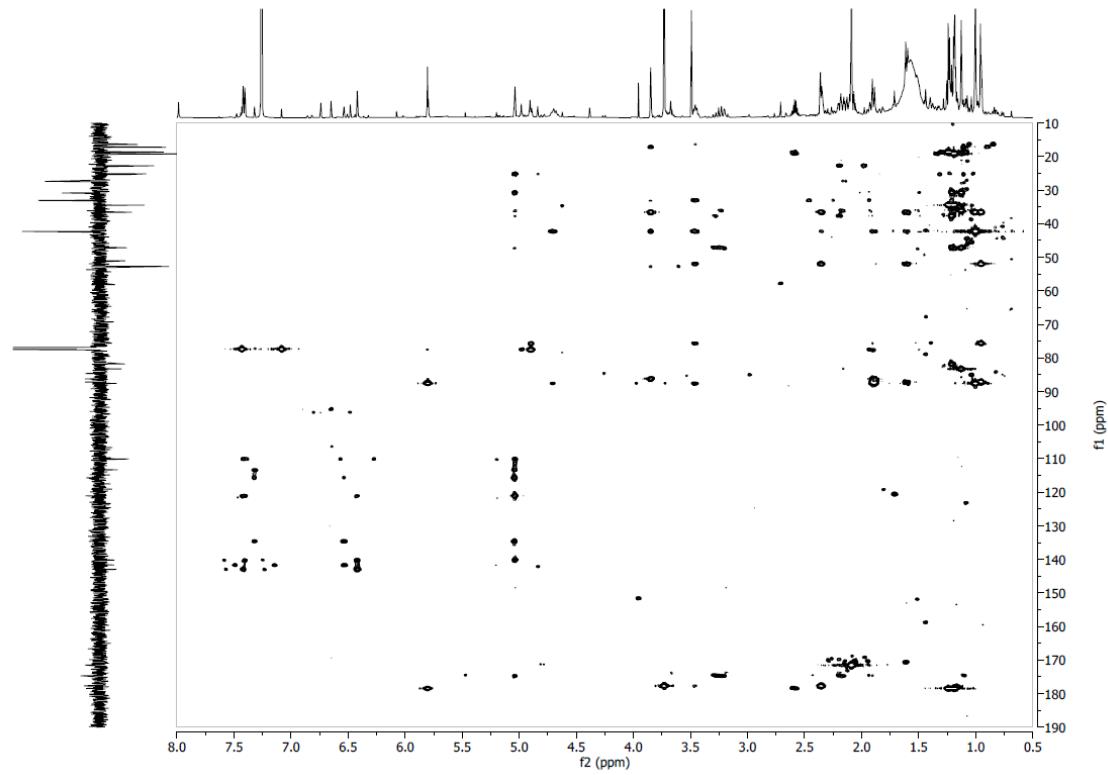
Supplementary Figure S4.2.35. COSY NMR spectrum of compound **6** in CDCl_3



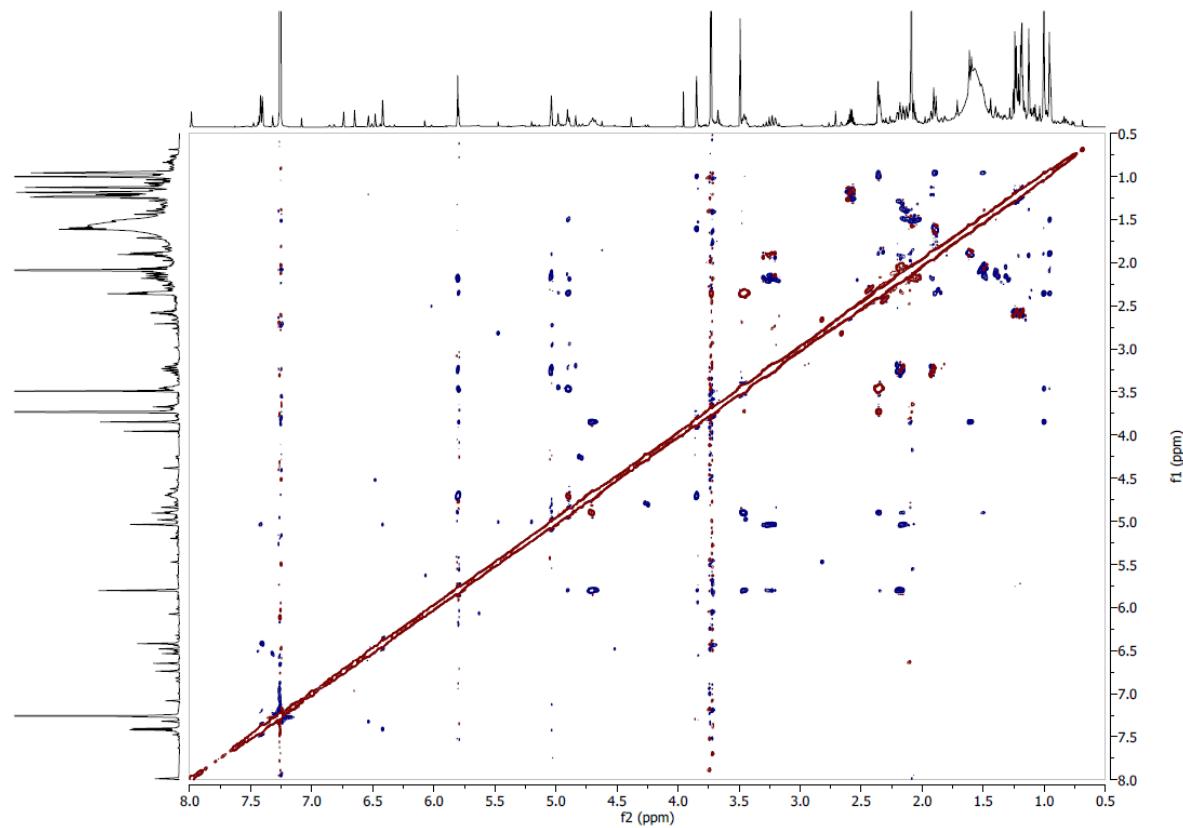
Supplementary Figure S4.2.36. ^{13}C -DEPTQ NMR spectrum of compound 6 in CDCl_3



Supplementary Figure S4.2.37. Edited HSQC NMR spectrum of compound 6 in CDCl_3

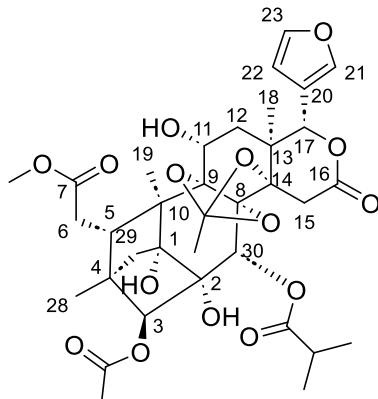


Supplementary Figure S4.2.38. HMBC NMR spectrum of compound **6** in CDCl_3



Supplementary Figure S4.2.39. ROESY NMR spectrum of compound **6** in CDCl_3

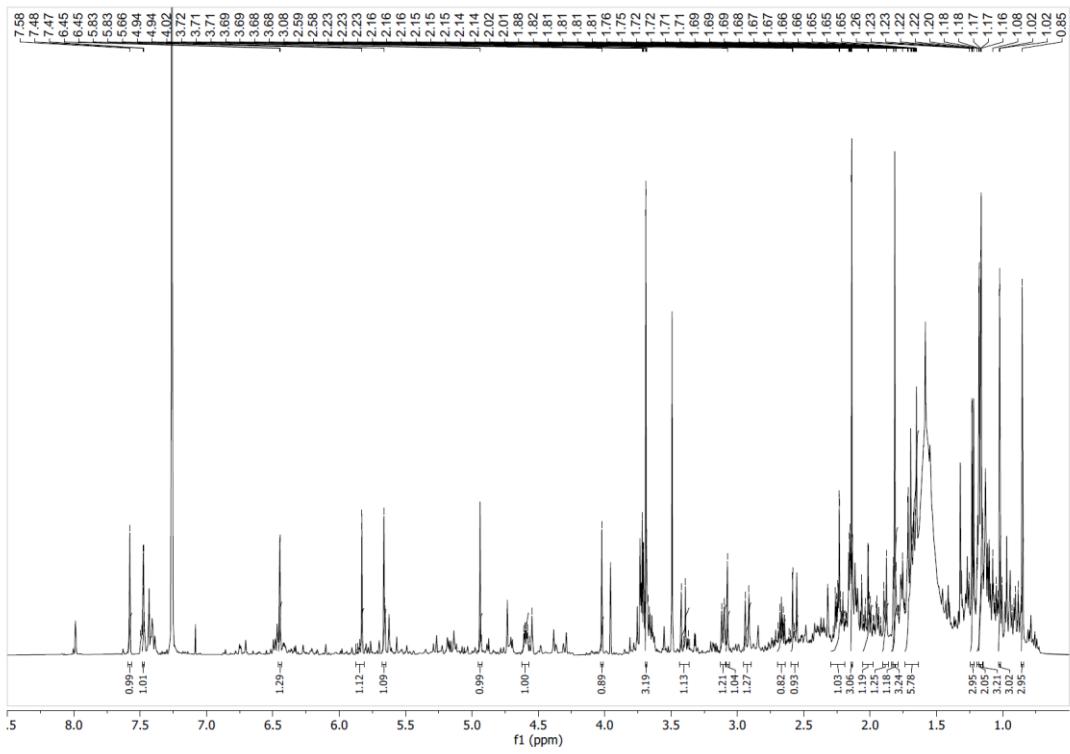
Compound 7. Amorphous white powder, HRESIMS m/z 727.2567 [M+Na]⁺ (calculated for C₃₅H₄₄O₁₅Na, error -0.64 ppm), 703.2604 [M-H]⁻ (calculated for C₃₅H₄₃O₁₅, error 1.28 ppm); $[\alpha]_D^{20}$ -23 (c 0.0013 CHCl₃); UV (c 0.0013, MeOH) λ_{max} 200 nm.



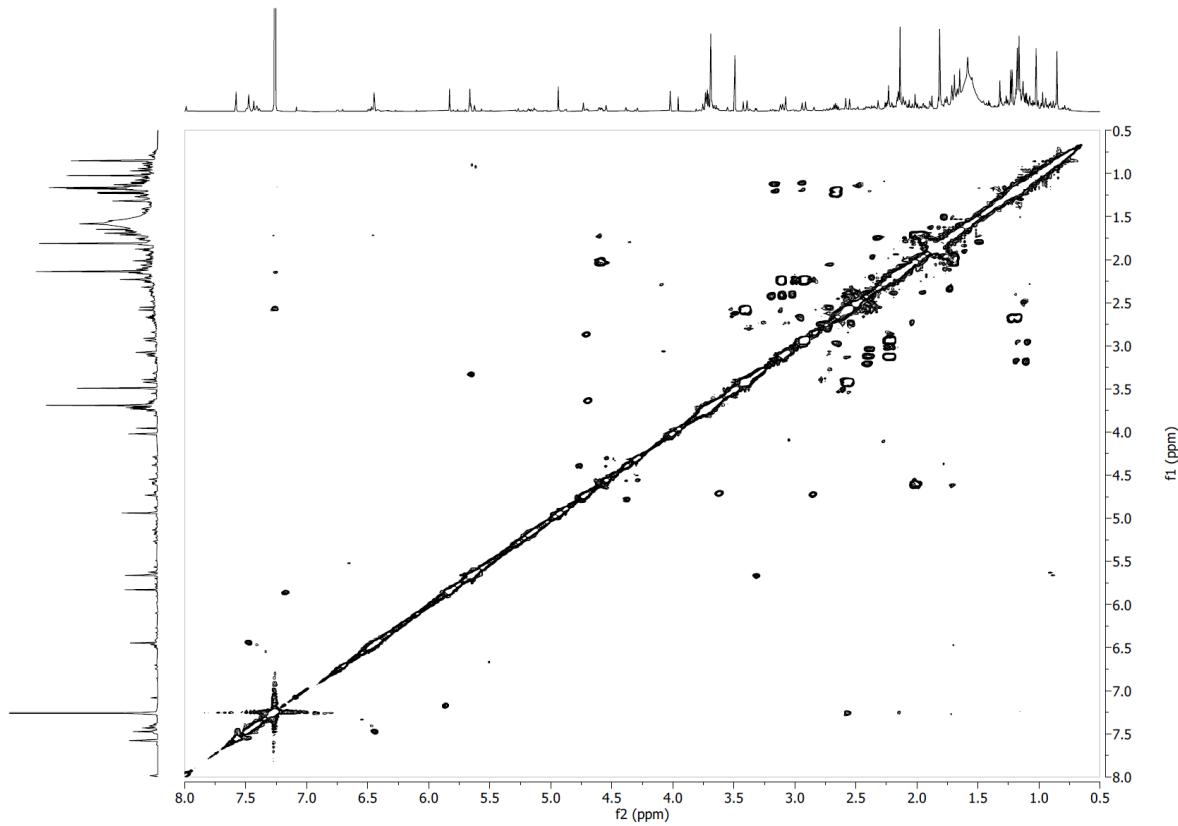
Chemical Formula: C₃₅H₄₄O₁₅

Exact Mass: 704.27

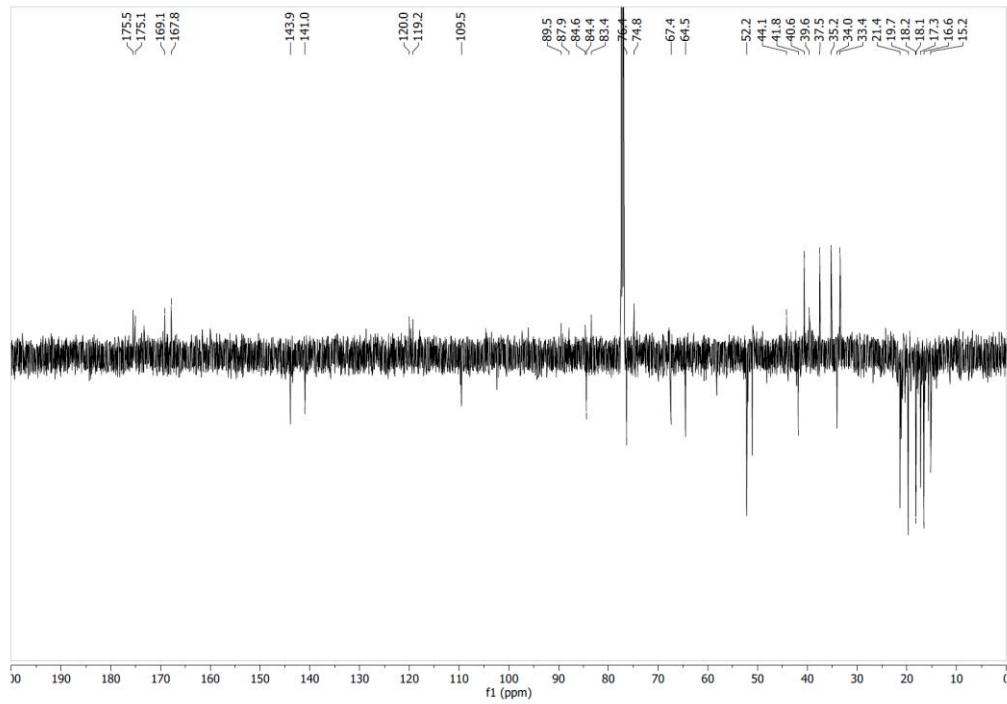
¹H NMR (CDCl₃, 600 MHz) δ 0.85 (3H, s, H₃-28), 1.02 (3H, s, H₃-18), 1.16 (3H, s, H₃-19), 1.17 (3H, d, J = 7.2 Hz, H₃-30d), 1.23 (3H, d, J = 7.2 Hz, H₃-30c), 1.68 (1H, m, H-12 β), 1.81 (3H, s, H₃-34), 1.82 (1H, d, J = 11.1 Hz, H-29''), 1.89 (1H, d, J = 11.1 Hz, H-29'), 2.02 (1H, t, J = 11.9 Hz, H-12 α), 2.14 (3H, s, H₃-3b), 2.23 (1H, dd, J = 16.6, 10.6 Hz, H-6''), 2.57 (1H, d, J = 18.8 Hz, H-15 α), 2.67 (1H, hept, J = 7.2 Hz, H-30b), 2.93 (1H, d, J = 16.6 Hz, H-6'), 3.08 (1H, s, OH-2), 3.11 (1H, d, J = 10.6 Hz, H-5), 3.41 (1H, d, J = 18.8 Hz, H-15 β), 3.69 (3H, s, OCH₃), 4.02 (1H, s, OH-1), 4.59 (1H, dd, J = 11.9, 5.1 Hz, H-11), 4.94 (1H, s, H-3), 5.66 (1H, s, H-17), 5.83 (1H, s, H-30), 6.45 (1H, d, J = 1.6 Hz, H-22), 7.48 (1H, d, J = 1.6 Hz, H-23), 7.58 (1H, s, H-21); ¹³C NMR (CDCl₃, 151 MHz) δ 15.2 (CH₃-28), 16.6 (CH₃-34), 17.3 (CH₃-19), 18.1 (CH₃-18), 18.2 (CH₃-30d), 19.7 (CH₃-30c), 21.4 (CH₃-3b), 33.4 (CH₂-6), 34.0 (CH-30b), 35.2 (CH₂-12), 37.5 (CH₂-15), 39.6 (C-13), 40.6 (CH₂-29), 41.8 (CH-5), 44.1 (C-4), 52.2 (OCH₃), 64.5 (CH-30), 67.4 (CH-11), 74.8 (C-2), 76.4 (CH-17), 83.4 (C-14), 84.4 (CH-3), 84.6 (C-1), 87.9 (C-9), 89.5 (C-8), 109.5 (C-22), 119.2 (C-33), 120.0 (C-20), 141.0 (CH-21), 143.9 (CH-23), 167.8 (C-16), 169.1 (C-3a), 175.1 (C-30a), 175.5 (C-7). Supplementary Figures S4.2.40-S4.2.45.



Supplementary Figure S4.2.40. ^1H NMR spectrum of compound **7** in CDCl_3 at 600 MHz

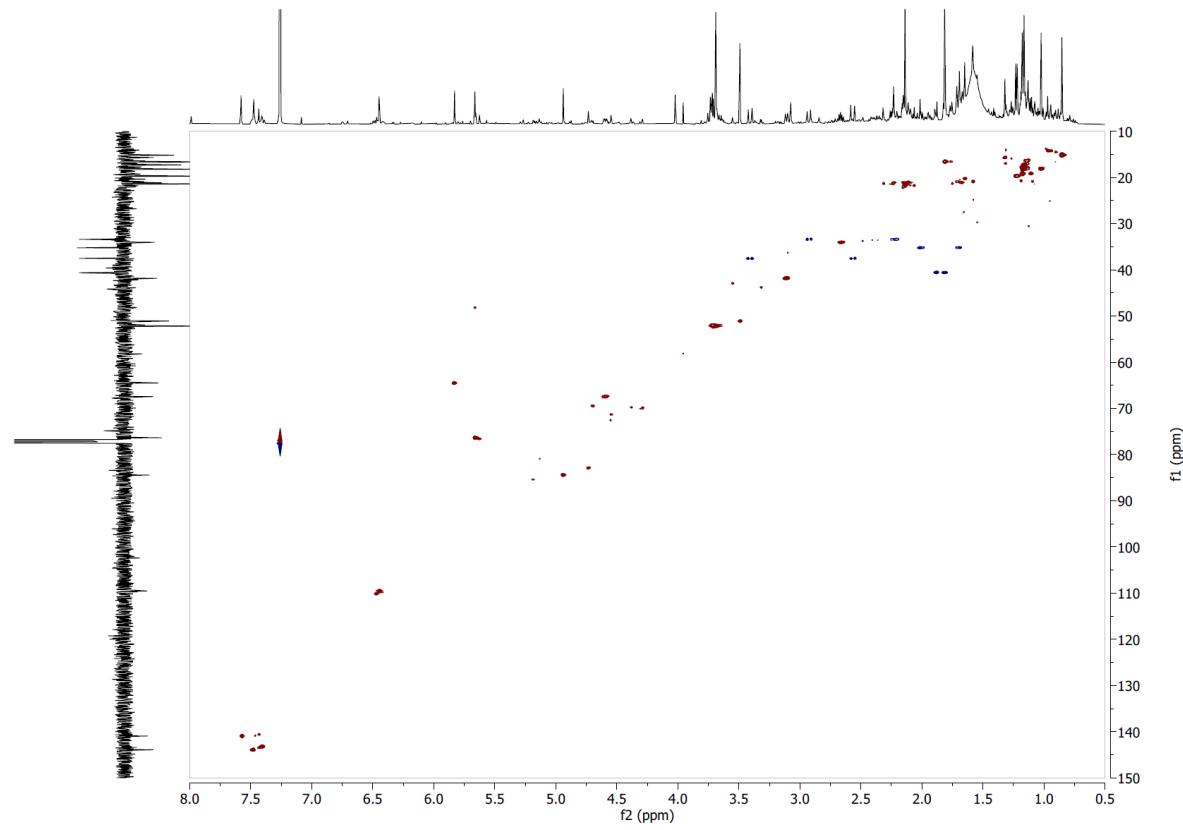


Supplementary Figure S4.2.41. COSY NMR spectrum of compound **7** in CDCl_3

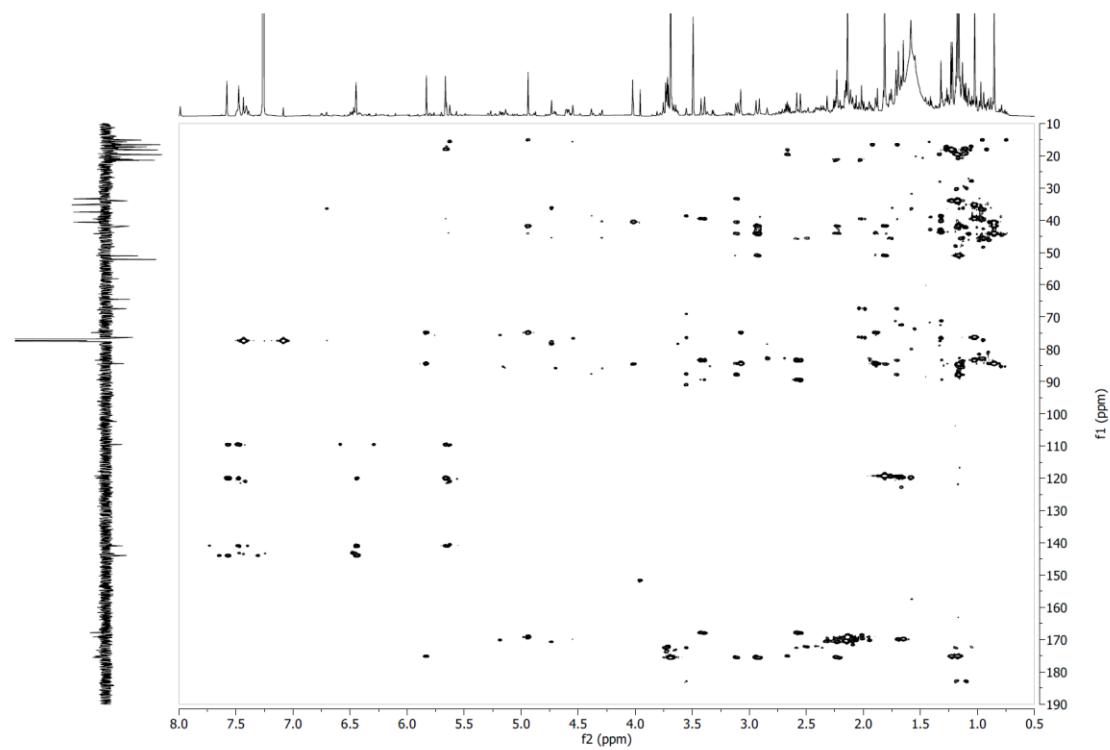


Supplementary

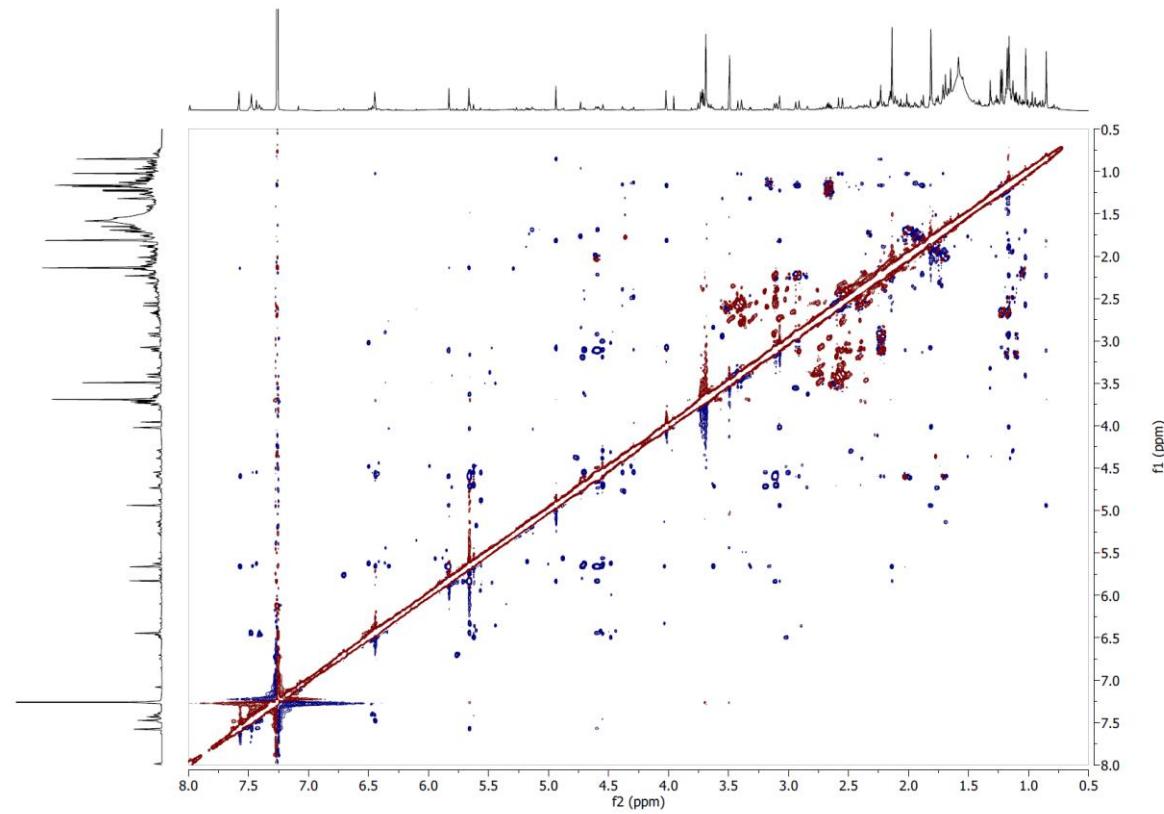
Figure S4.2.42. ^{13}C -DEPTQ NMR spectrum of compound 7 in CDCl_3 at 151 MHz



Supplementary Figure S4.2.43. Edited HSQC NMR spectrum of compound 7 in CDCl_3

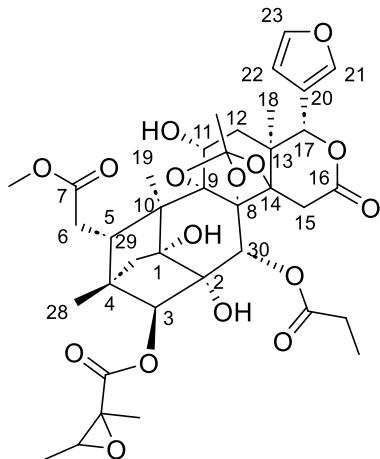


Supplementary Figure S4.2.44. HMBC NMR spectrum of compound 7 in CDCl_3



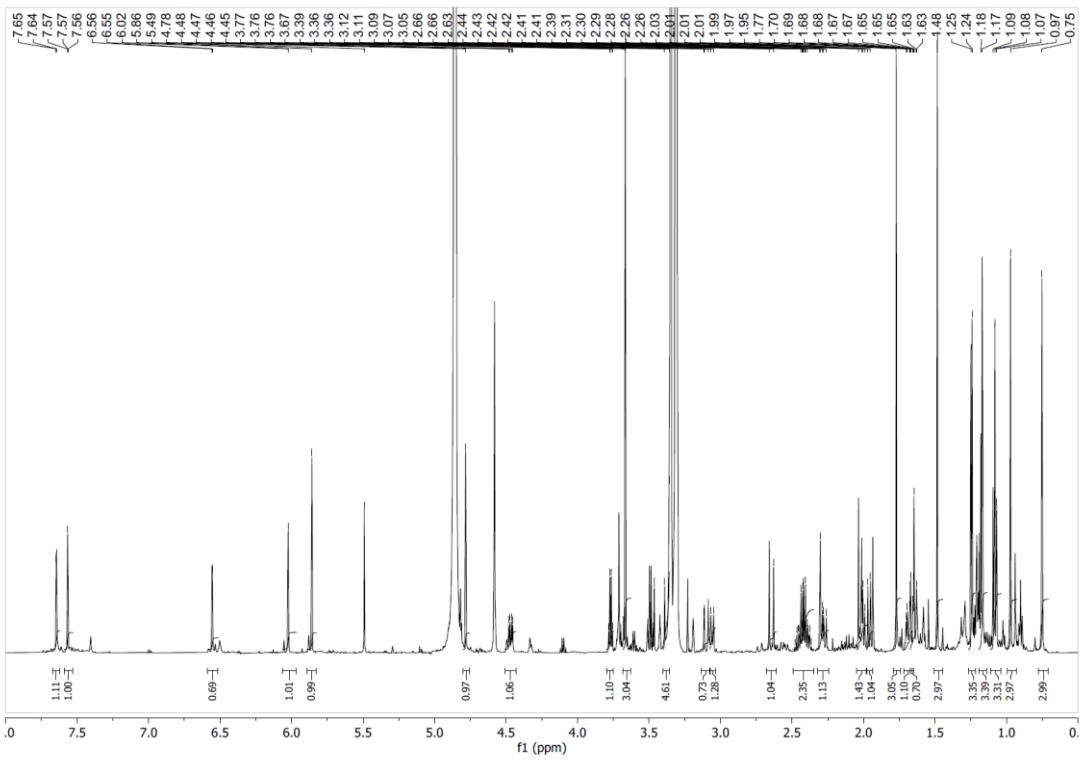
Supplementary Figure S4.2.45. ROESY NMR spectrum of compound 7 in CDCl_3

Compound 8. Amorphous white powder, HRESIMS m/z 747.2865 [M+H]⁺ (calculated for C₃₇H₄₇O₁₆, error 0.93 ppm), 745.2713 [M-H]⁻ (calculated for C₃₇H₄₅O₁₆, error 1.54 ppm); $[\alpha]_D^{20}$ -9 (c 0.0013 CHCl₃); UV (c 0.013, MeOH) λ_{max} 200 nm.

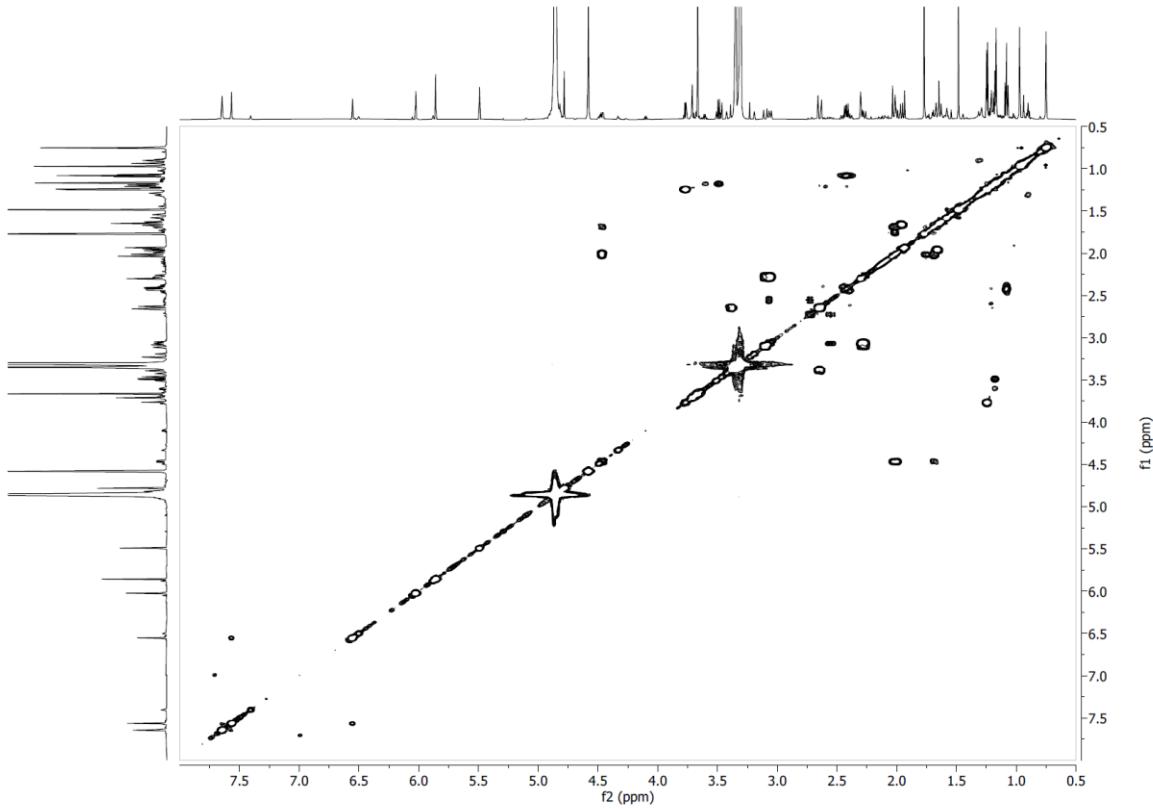


Chemical Formula: C₃₇H₄₆O₁₆
Exact Mass: 746.28

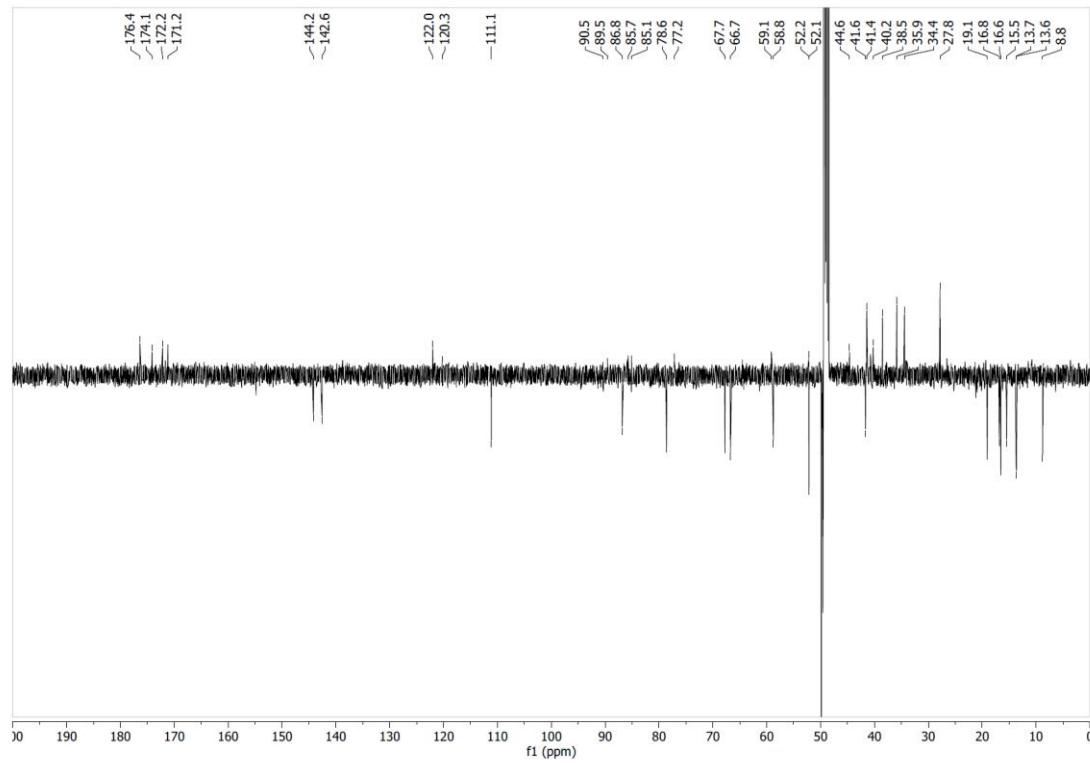
¹H NMR (CD₃OD, 600 MHz) δ 0.75 (3H, s, H₃-28), 0.97 (3H, s, H₃-18), 1.08 (3H, t, J = 7.5 Hz, H₃-30c), 1.17 (3H, s, H₃-19), 1.25 (3H, d, J = 5.3 Hz, H₃-3d), 1.48 (3H, s, H₃-3e), 1.66 (1H, d, J = 11.0 Hz, H-29¹¹), 1.69 (1H, dd, J = 13.0, 4.8 Hz, H-12 β), 1.77 (3H, s, H₃-34), 1.96 (1H, d, J = 11.0 Hz, H-29¹), 2.01 (1H, t, J = 13.0, 11.9 Hz, H-12 α), 2.28 (1H, dd, J = 16.9, 11.1 Hz, H-6¹¹), 2.43 (2H, m, H₂-30b), 2.64 (1H, d, J = 18.8 Hz, H-15 α), 3.06 (1H, d, J = 11.1 Hz, H-5), 3.10 (1H, d, J = 16.9 Hz, H-6¹), 3.37 (1H, d, J = 18.8 Hz, H-15 β), 3.67 (3H, s, OCH₃), 3.77 (1H, q, J = 5.3 Hz, H-3c), 4.47 (1H, dd, J = 11.9, 4.8 Hz, H-11), 4.78 (1H, s, H-3), 5.86 (1H, s, H-30), 6.02 (1H, s, H-17), 6.55 (1H, t, J = 1.7 Hz, H-22), 7.57 (1H, t, J = 1.7 Hz, H-23), 7.64 (1H, d, J = 1.7 Hz, H-21); ¹³C NMR (MeOD, 151 MHz) δ 8.8 (CH₃-30c), 13.6 (CH₃-3d), 13.7 (CH₃-3e), 15.5 (CH₃-28), 16.6 (CH₃-34), 16.8 (CH₃-19), 19.1 (CH₃-18), 27.8 (CH₃-30b), 34.4 (CH₂-6), 35.9 (CH₂-12), 38.5 (CH₂-15), 40.2 (C-13), 41.4 (CH₂-29), 41.6 (CH-5), 44.6 (C-4), 52.1 (OCH₃), 52.2 (C-10), 58.8 (CH-3c), 59.1 (C-3b), 66.7 (CH-30), 67.7 (CH-11), 77.2 (C-2), 78.6 (CH-17), 85.1 (C-14), 85.7 (C-1), 86.8 (CH-3), 89.5 (C-9), 90.5 (C-8), 111.1 (CH-22), 120.3 (C-33), 122.0 (C-20), 142.6 (CH-21), 144.2 (CH-23), 171.2 (C-16), 172.2 (C-3a), 174.1 (C-30a), 176.4 (C-7). Supplementary Figures S4.2.46-S4.2.51.



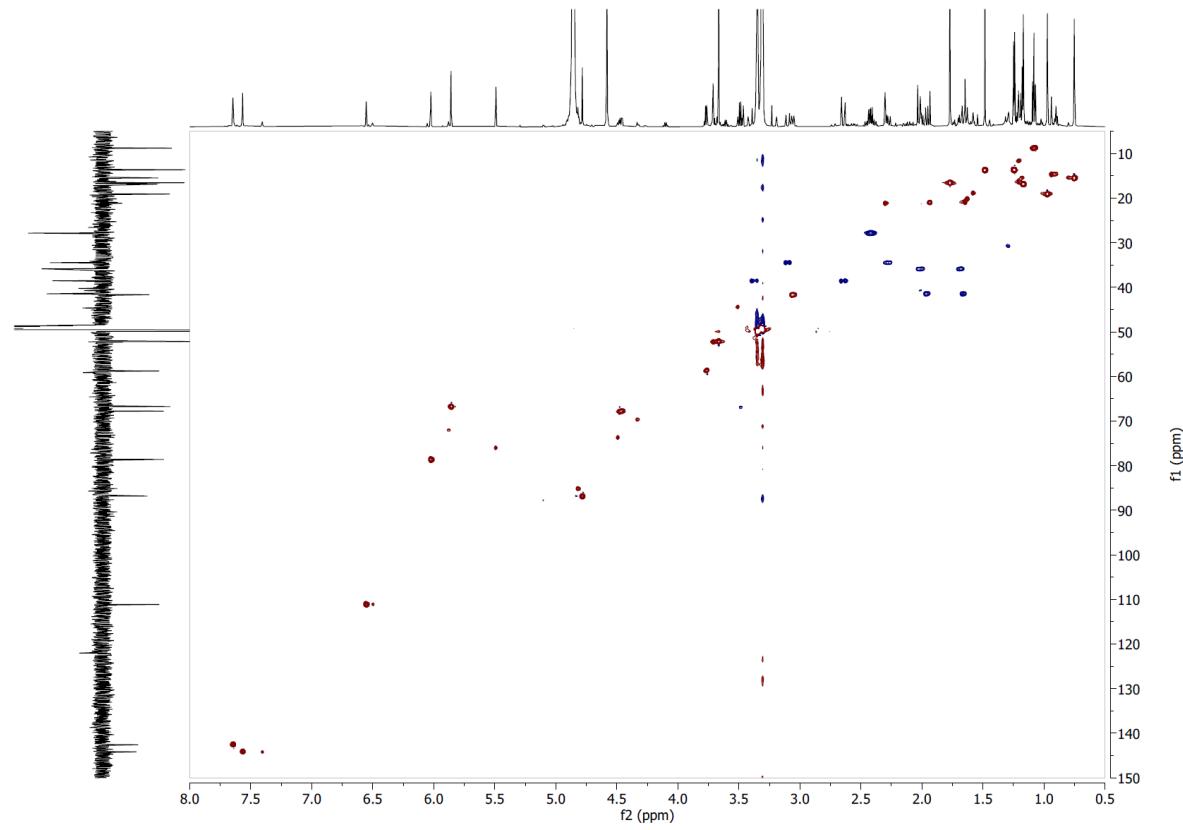
Supplementary Figure S4.2.46. ^1H NMR spectrum of compound **8** in CD_3OD at 600 MHz



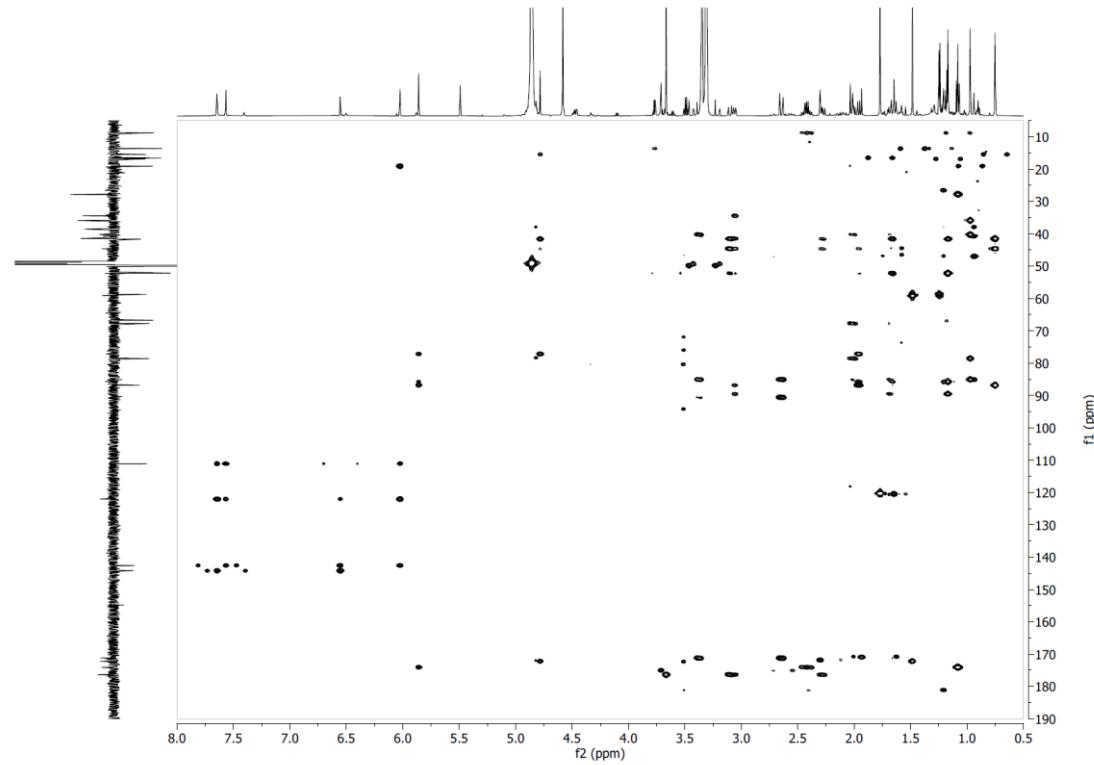
Supplementary Figure S4.2.47. COSY NMR spectrum of compound **8** in CD_3OD



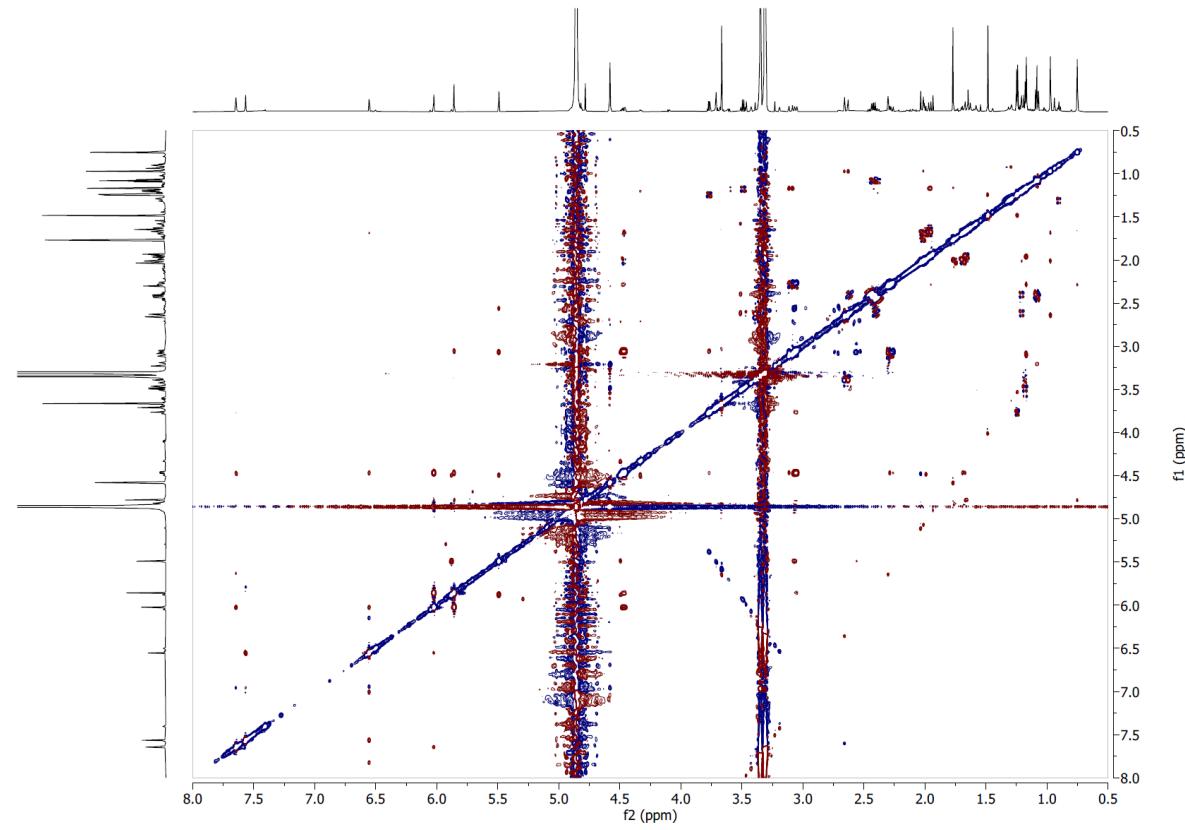
Supplementary Figure S4.2.47. ^{13}C -DEPTQ NMR spectrum of compound **8** in CD_3OD at 151 MHz



Supplementary Figure S4.2.49. Edited HSQC NMR spectrum of compound **8** in CD_3OD

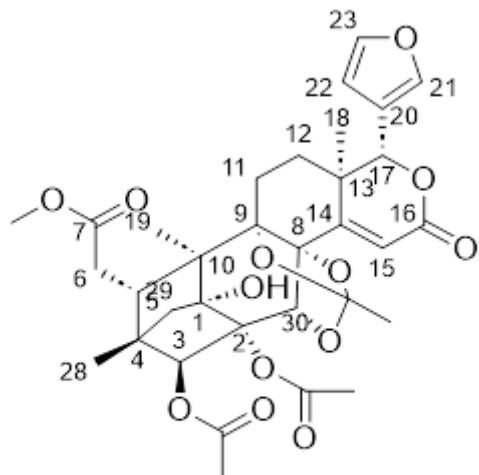


Supplementary Figure S4.2.50. HMBC NMR spectrum of compound **8** in CD_3OD



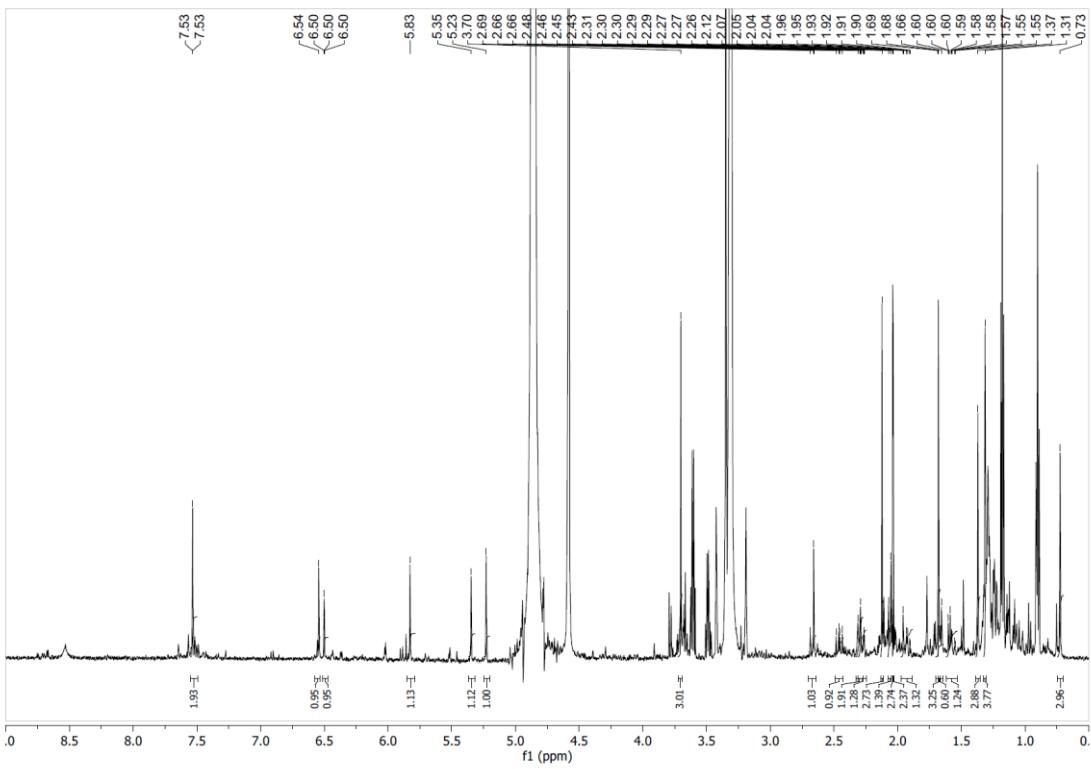
Supplementary Figure S4.2.51. ROESY NMR spectrum of compound **8** in CD_3OD

Compound 9: Moluccensin Y [68]. Amorphous white powder, HRESIMS m/z 643.2384 [$M+H$]⁺ (calculated for C₃₃H₃₉O₁₃, error -0.09 ppm); $[\alpha]_D^{20} -0.3$ (c 0.0006 CHCl₃); UV (c 0.006, MeOH) λ_{max} 200 nm.

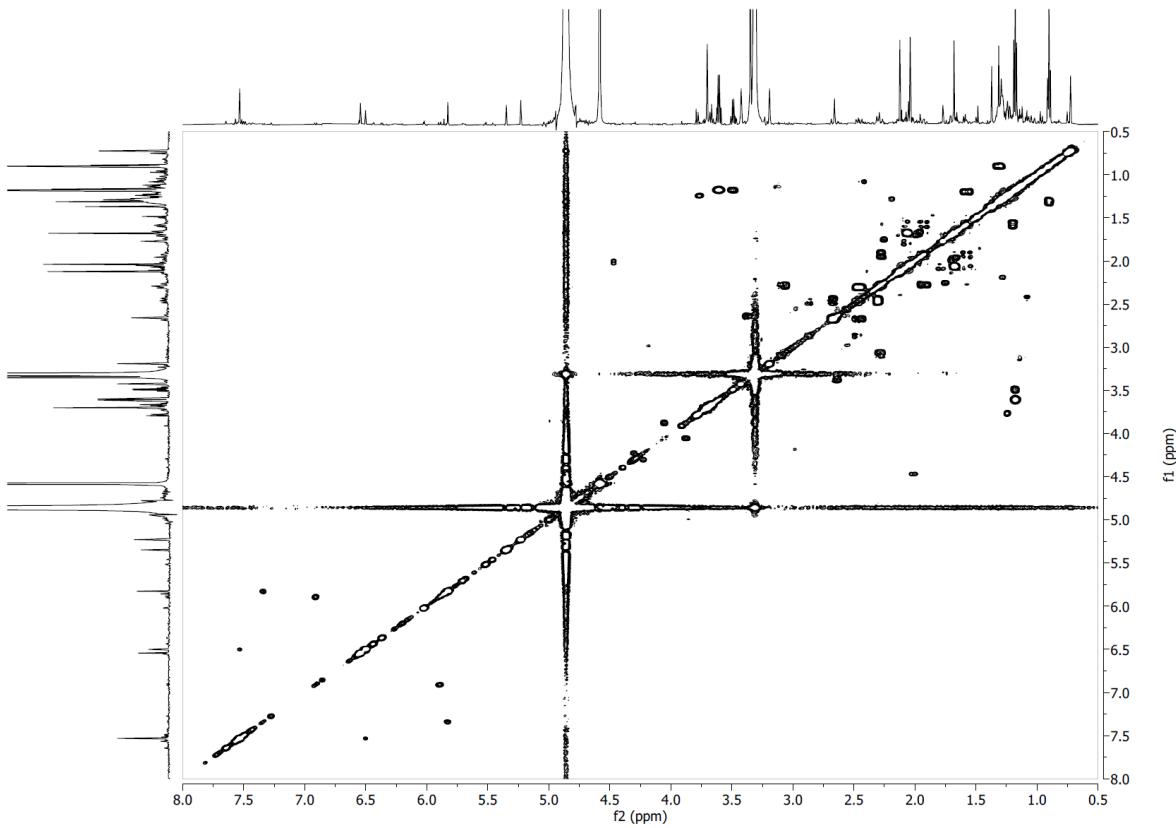


Chemical Formula: C₃₃H₃₈O₁₃
Exact Mass: 642.23

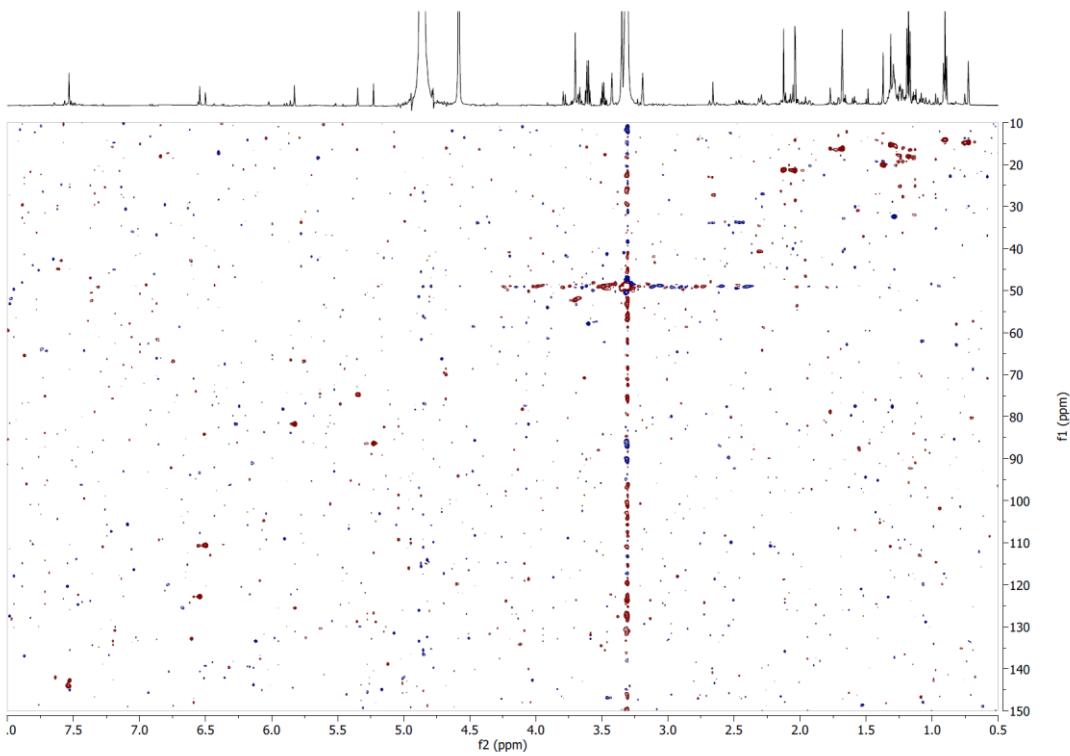
¹H NMR (CD₃OD, 600 MHz) δ 0.73 (3H, s, H₃-28), 1.19 (1H, overlapped, H-12a), 1.31 (3H, s, H₃-19), 1.37 (3H, s, H₃-18), 1.58 (1H, td, J = 15.7, 3.8 Hz, H-12 β), 1.67 (1H, d, J = 11.9 Hz, H-29'), 1.68 (3H, s, H₃-34), 1.93 (1H, td, J = 15.7, 4.4 Hz, H-11 α), 2.04 (3H, s, H₃-3b), 2.06 (1H, d, J = 11.9 Hz, H-29'), 2.12 (3H, s, H₃-2b), 2.28 (1H, d, J = 15.7 Hz, H-11 β), 2.30 (2H, d, J = 12.0 Hz, H-5), 2.46 (1H, dd, J = 17.1, 12.0 Hz, H-6'), 2.67 (1H, d, J = 17.1 Hz, H-6'), 3.70 (3H, s, OCH₃), 5.23 (1H, s, H-3), 5.35 (1H, s, H-30), 5.83 (1H, s, H-17), 6.50 (1H, t, J = 1.4 Hz, H-22), 6.54 (1H, s, H-15), 7.53 (2H, d, J = 1.4 Hz, H-21, H-23); ¹³C NMR (CD₃OD, 151 MHz) δ 14.6 (CH₃-28), 15.3 (CH₃-19), 16.2 (CH₃-34), 20.1 (CH₃-18), 21.3 (CH₃-2b), 21.5 (CH₃-3b), 26.9 (CH₂-11), 30.1 (CH₂-12), 33.8 (CH₂-6), 38.9 (C-13), 40.1 (CH₂-29), 40.6 (CH-5), 45.6 (C-4), 52.2 (OCH₃), 74.7 (CH-30), 81.8 (CH-17), 84.9 (C-8), 85.2 (C-1), 86.3 (CH-3), 87.4 (C-9), 110.6 (CH-22), 120.7 (C-20), 120.9 (C-33), 122.7 (C-15), 142.8 (CH-21), 144.2 (CH-23), 156.8 (C-14), 165.8 (C-16), 170.1 (C-3a), 171.9 (C-2a), 175.5 (C-7). Supplementary Figures S4.2.52-S4.2.56.



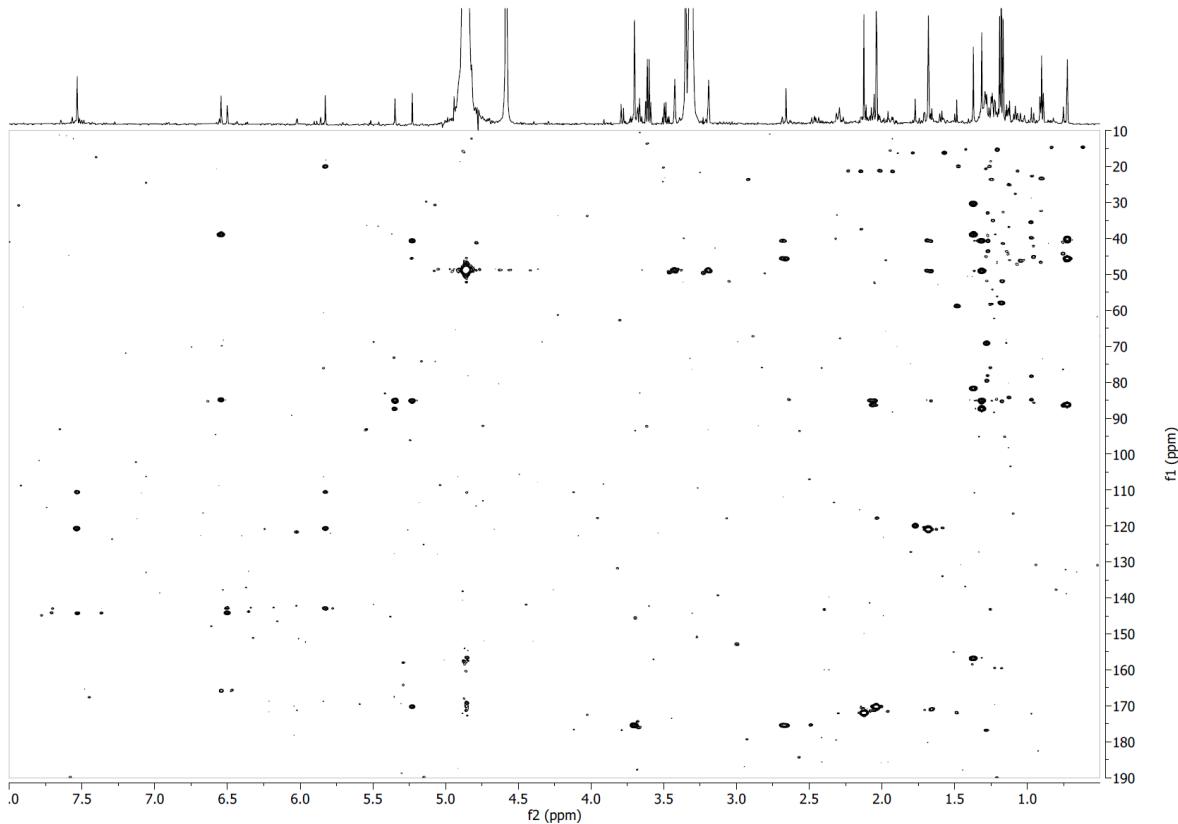
Supplementary Figure S4.2.52. ^1H NMR spectrum of compound **9** in CD_3OD at 600 MHz



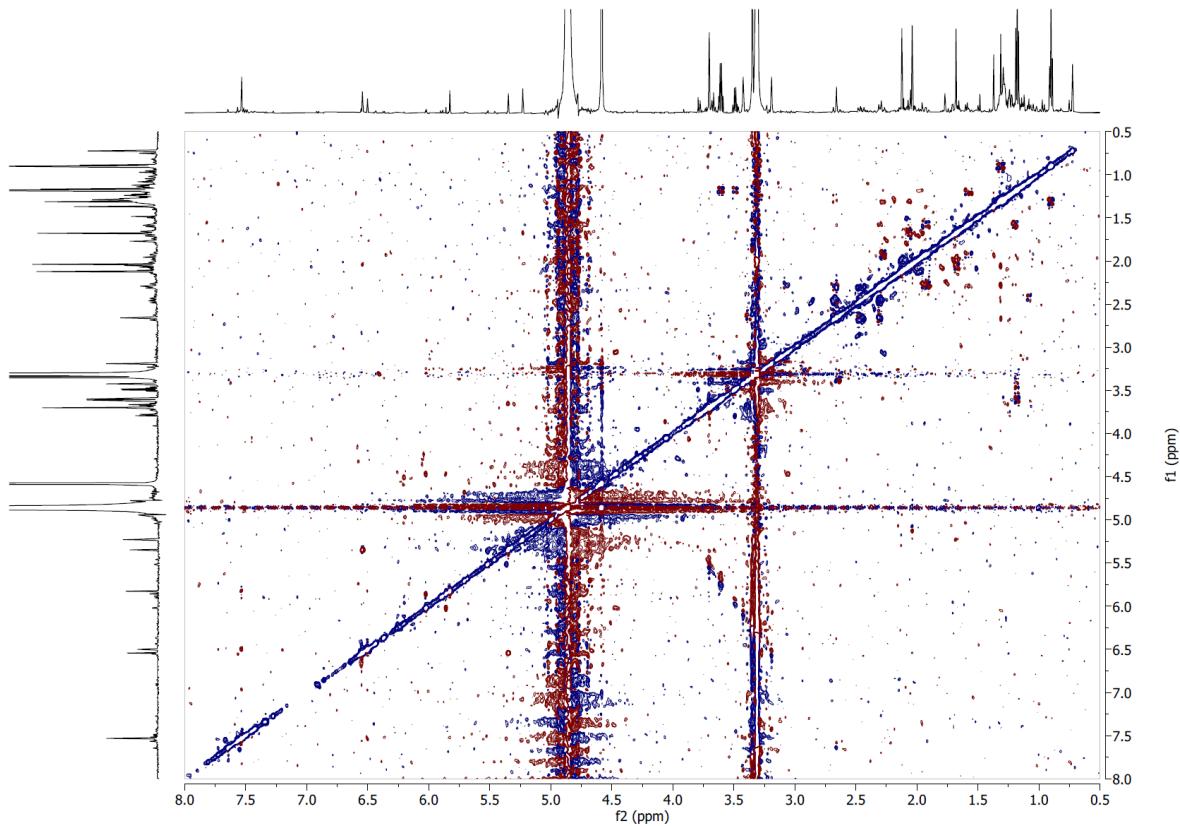
Supplementary Figure S4.2.53. COSY NMR spectrum of compound **9** in CD_3OD



Supplementary Figure S4.2.54. Edited HSQC NMR spectrum of compound **9** in CD_3OD

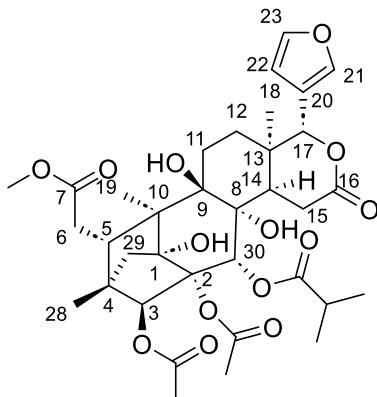


Supplementary Figure S4.2.55. HMBC NMR spectrum of compound **9** in CD_3OD



Supplementary Figure S4.2.56. ROESY NMR spectrum of compound 9 in CD_3OD

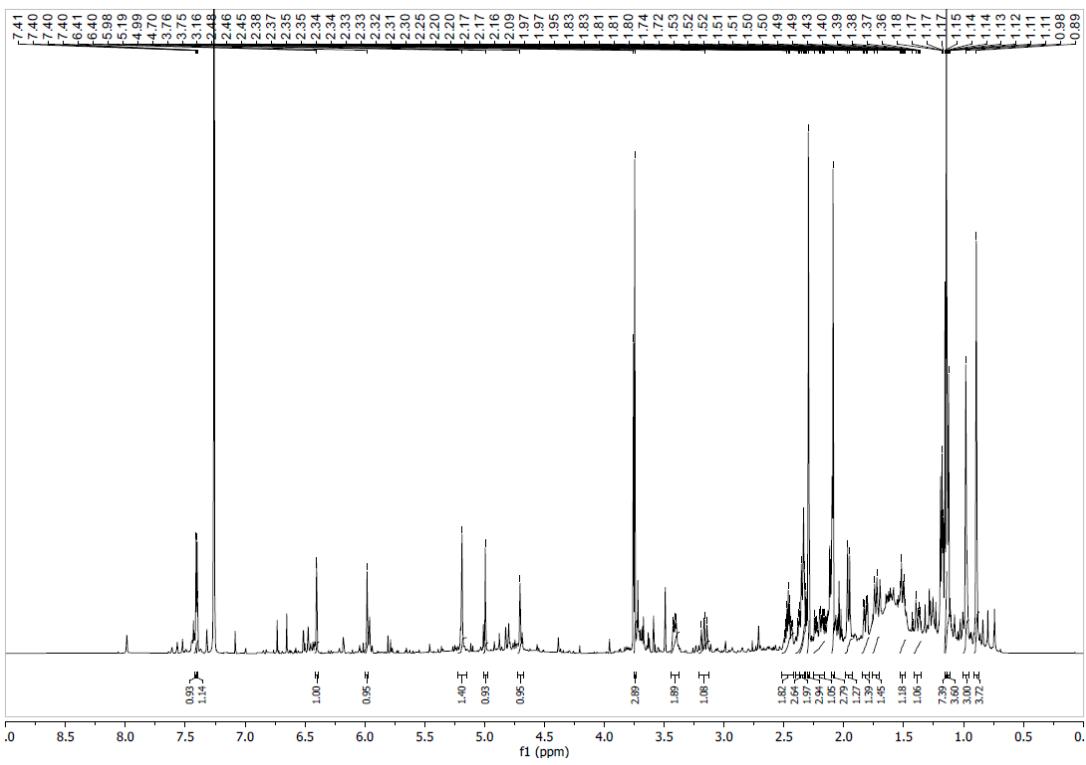
Compound **10** LQ021019: name. Amorphous white powder, HRESIMS m/z 691.2963 [$M+H]^+$ (calculated for $C_{35}H_{47}O_{14}$, error 0.43 ppm), 689.2811 [$M-H]^-$ (calculated for $C_{35}H_{45}O_{14}$, error 1.08 ppm); $[\alpha]_D^{20} 0.46$ (c 0.0016 CHCl₃); UV (c 0.0016, MeOH) λ_{max} 233, 282 nm.



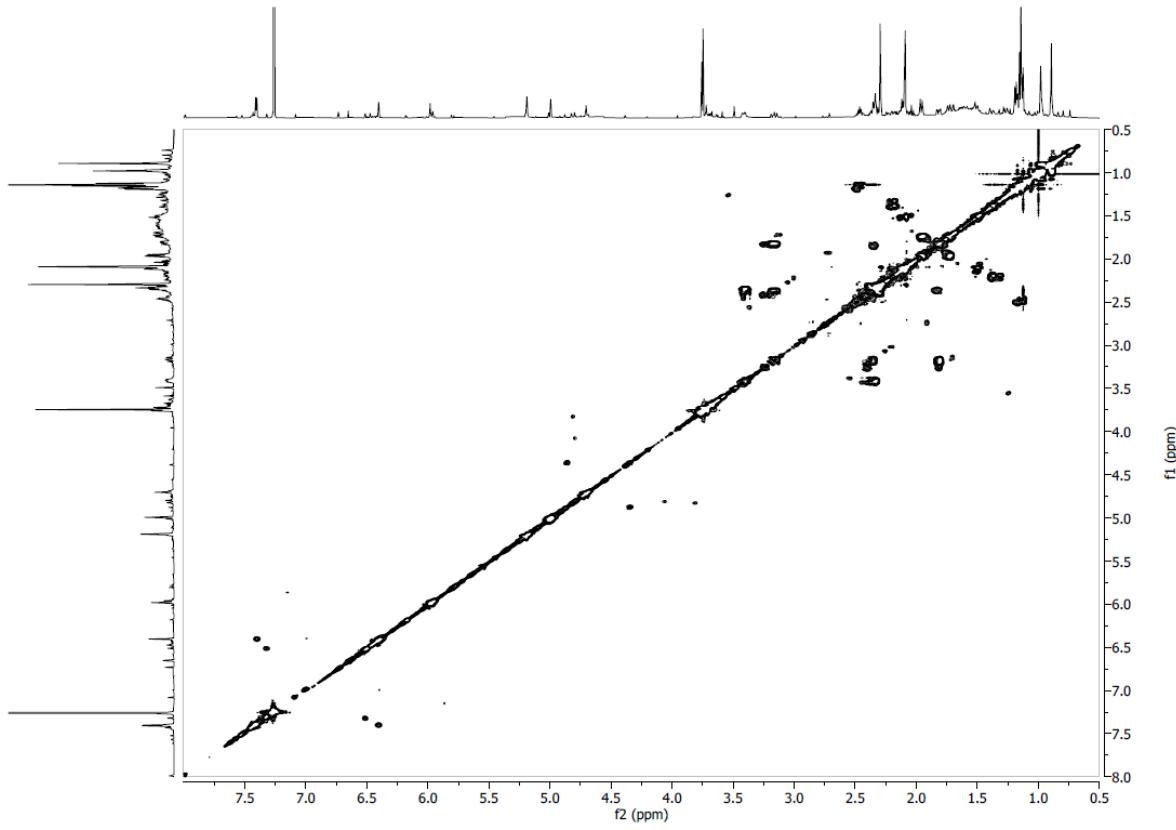
Chemical Formula: $C_{35}H_{46}O_{14}$

Exact Mass: 690.29

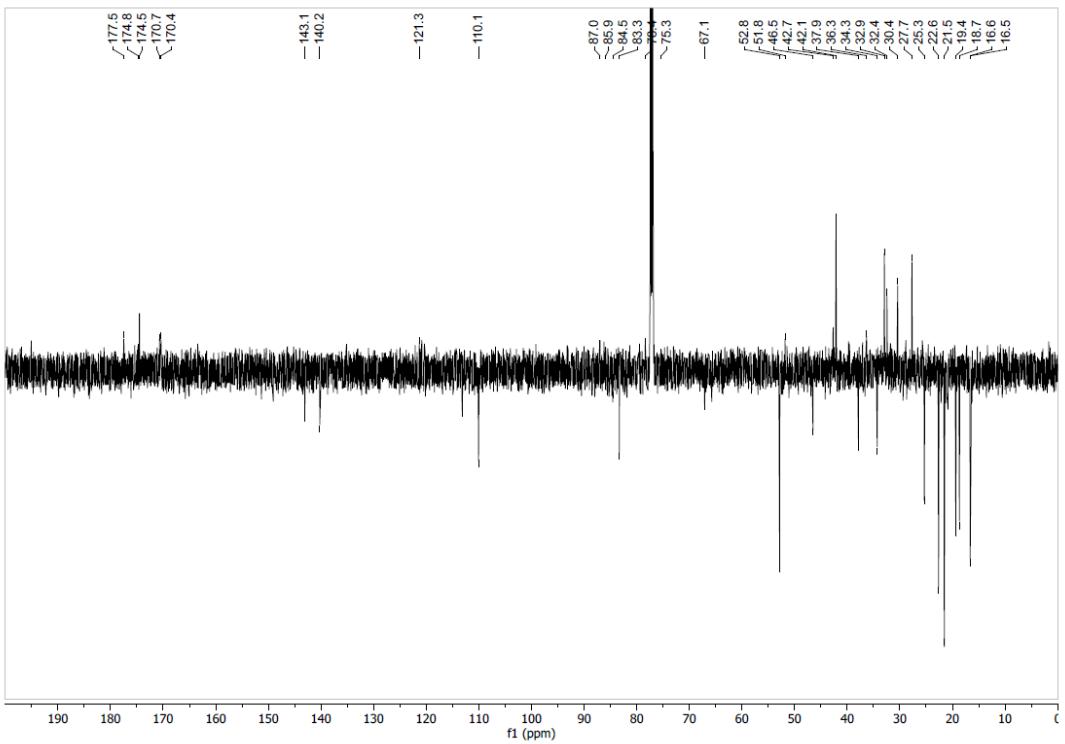
¹H NMR (CDCl₃, 600 MHz) δ 0.89 (3H, s, H₃-28), 0.98 (3H, s, H₃-19), 1.13 (3H, d, J = 7.0 Hz, H₃-30d), 1.14 (3H, s, H₃-18), 1.15 (7H, d, J = 7.0 Hz, H₃-30c), 1.38 (1H, dt, J = 12.9, 3.9 Hz, H-12 α), 1.51 (1H, m, H-11 α), 1.73 (1H, d, J = 11.0 Hz, H-29*pro-R*), 1.82 (1H, dd, J = 12.1, 4.4 Hz, H-14), 1.96 (1H, d, J = 11.0 Hz, H-29*pro-S*), 2.09 (3H, s, H₃-2b), 2.20 (1H, td, J = 12.9, 3.9 Hz, H-12 β), 2.30 (3H, s, H₃-3b), 2.34 (2H, d, J = 11.8 Hz, H₂-6), 2.36 (1H, dd, J = 16.2, 4.4 Hz, H-15 α), 2.46 (1H, hept, J = 7.0 Hz, H₃-30b), 3.17 (1H, dd, J = 16.2, 12.1 Hz, H-15 β), 3.41 (1H, dd, J = 11.8, 5.1 Hz, H-5), 3.75 (3H, s, OCH₃), 4.70 (1H, s, OH-9), 4.99 (1H, s, H-17), 5.19 (1H, s, H-3), 5.98 (1H, s, H-30), 6.40 (1H, d, J = 1.8 Hz, H-22), 7.40 (1H, t, J = 1.8 Hz, H-23), 7.41 (1H, d, J = 1.8 Hz, H-21); ¹³C NMR (CDCl₃, 151 MHz) δ 16.5 (CH₃-19), 16.6 (CH₃-28), 18.7 (CH₃-30d), 19.4 (CH₃-30c), 21.5 (CH₃-3b), 22.6 (CH₃-2b), 25.3 (CH₃-18), 27.7 (CH₂-11), 30.4 (CH₂-12), 32.4 (CH₂-15), 32.9 (CH₂-6), 34.3 (CH-30b), 36.3 (C-13), 37.9 (CH-5), 42.1 (CH₂-29), 42.7 (C-4), 46.5 (CH-14), 51.8 (C-10), 52.8 (OCH₃), 67.1 (CH-30), 75.3 (C-9), 78.4 (C-8), 83.3 (CH-17), 84.5 (CH-3), 85.9 (C-2), 87.0 (C-1), 110.1 (CH-22), 121.3 (C-20), 140.2 (CH-21), 143.1 (CH-23), 170.4 (C-3a), 170.7 (C-2a), 174.5 (C-16), 174.8 (C-30a), 177.5 (C-7). **Supplementary Figures S4.2.57–S4.2.62.**



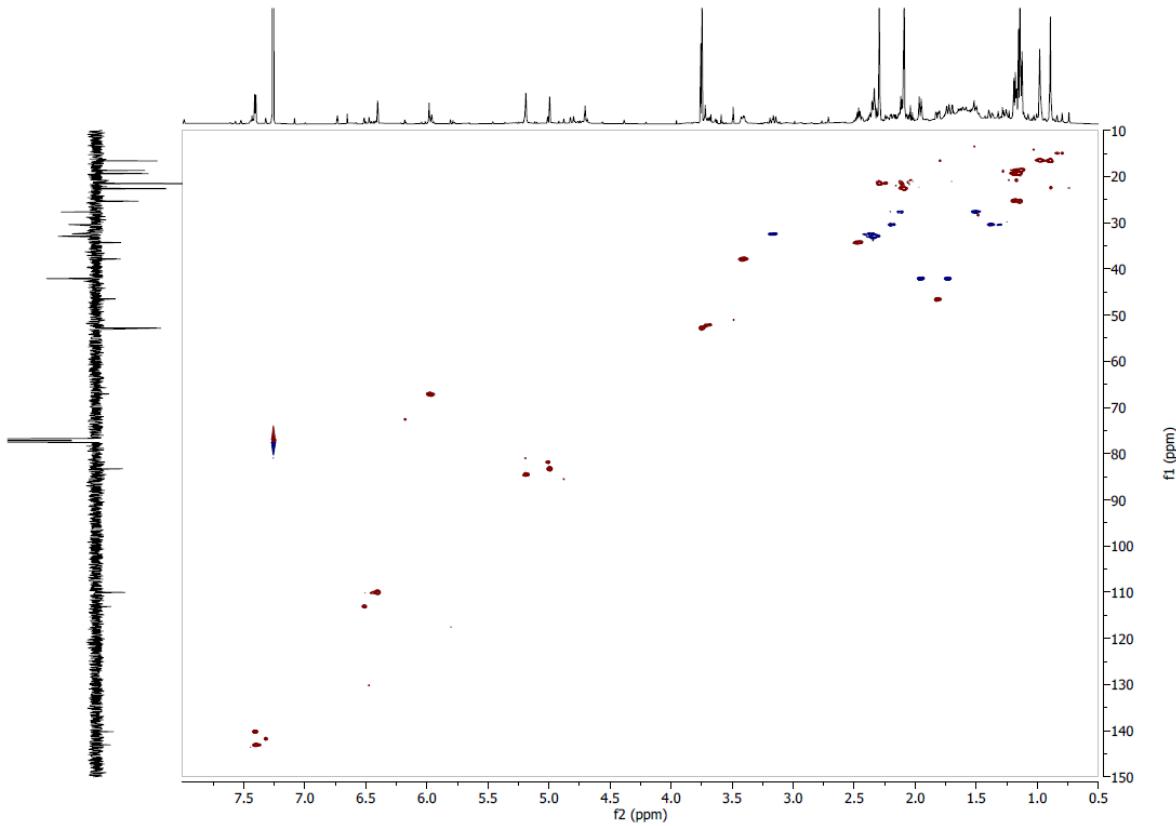
Supplementary Figure S4.2.57. ^1H NMR spectrum of compound **10** in CDCl_3 at 600 MHz



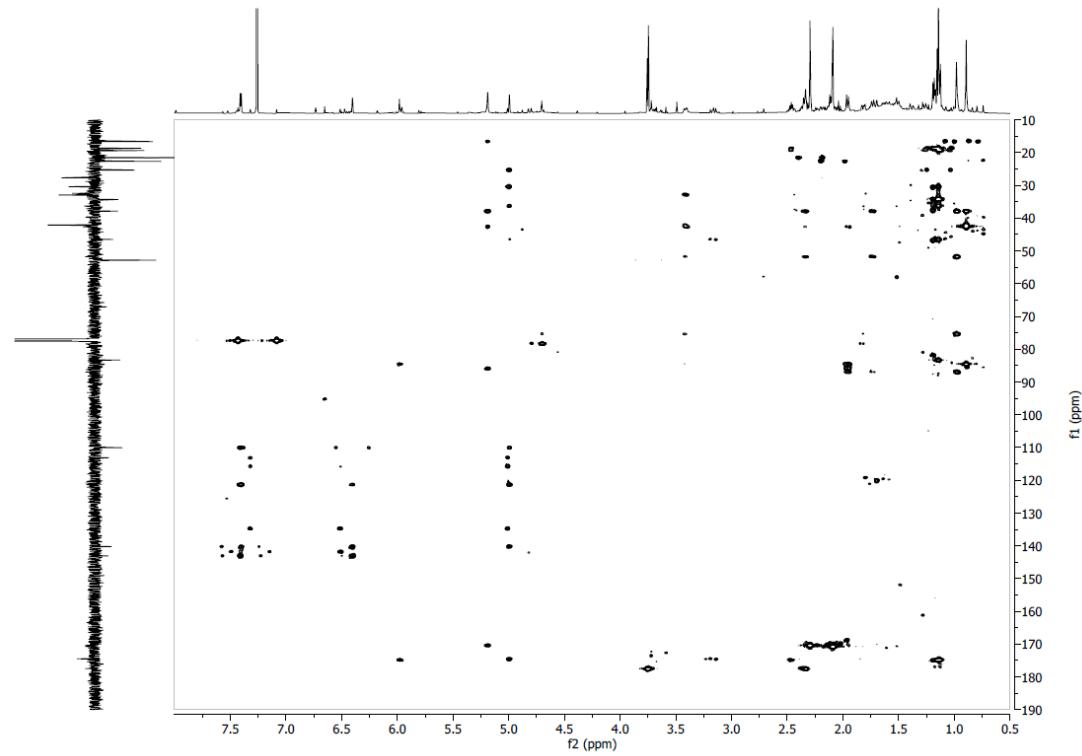
Supplementary Figure S4.2.58. COSY NMR spectrum of compound **10** in CDCl_3



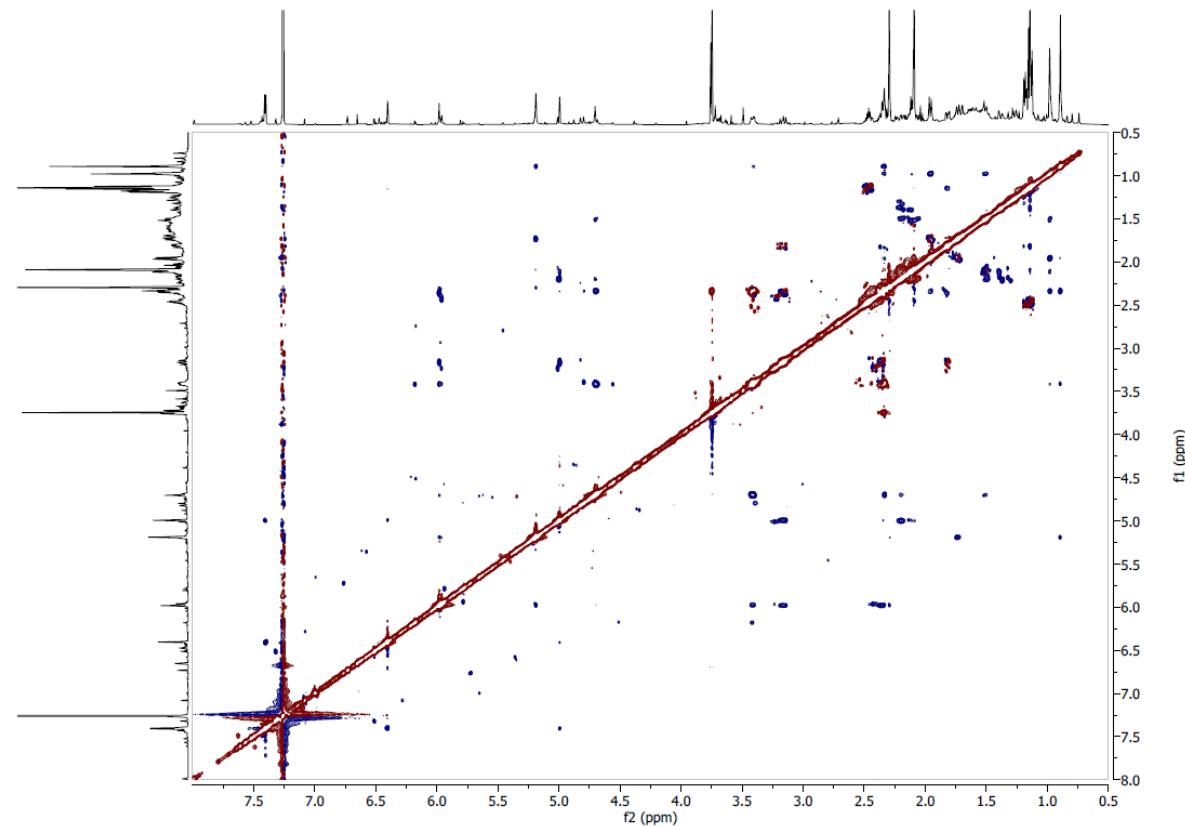
Supplementary Figure S4.2.59. ^{13}C -DEPTQ NMR spectrum of compound **10** in CDCl_3



Supplementary Figure S4.2.60. Edited HSQC NMR spectrum of compound **10** in CDCl_3

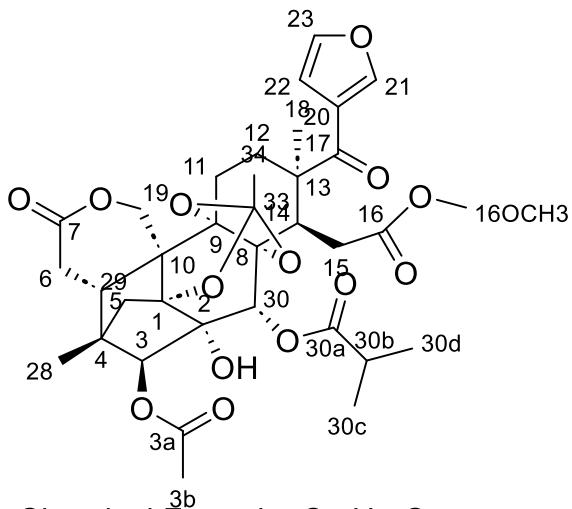


Supplementary Figure S4.2.61. HMBC NMR spectrum of compound **10** in CDCl_3



Supplementary Figure S4.2.62. ROESY NMR spectrum of compound **10** in CDCl_3

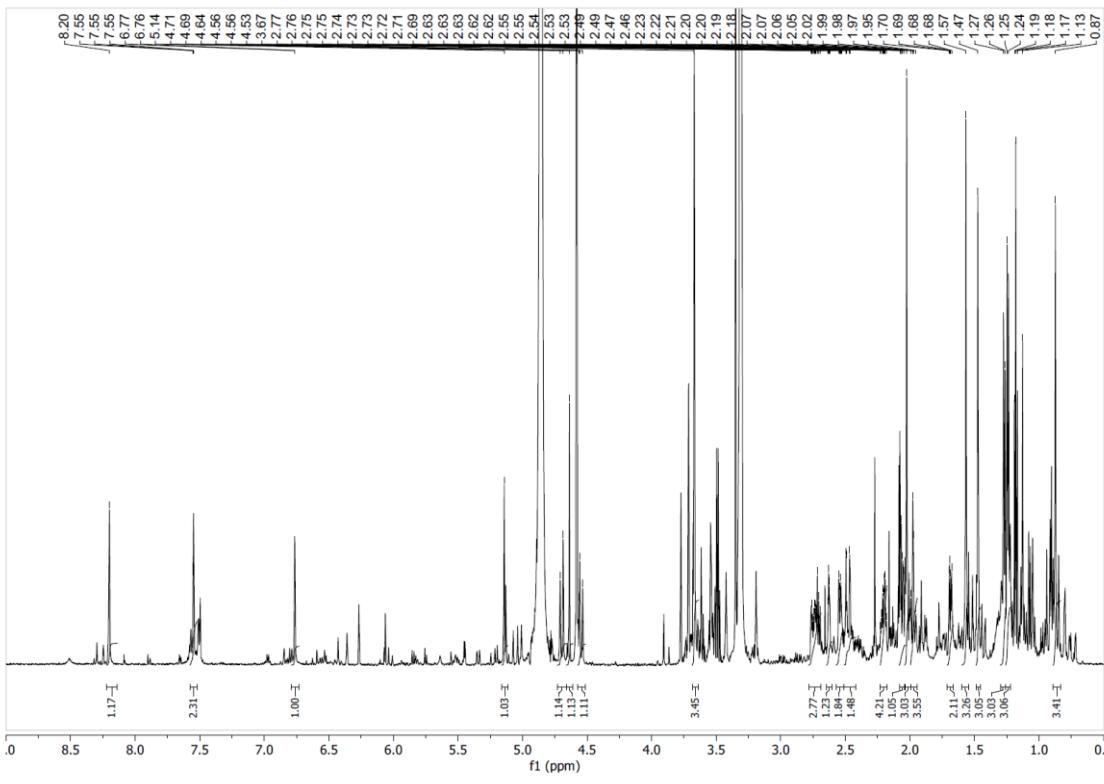
Compound 11. Amorphous white powder, HRESIMS m/z 687.2650 [M+H]⁺ (calculated for C₃₅H₄₃O₁₄, error 0.40 ppm), 685.2479 [M-H]⁻ (calculated for C₃₅H₄₁O₁₄, error -1.69 ppm); $[\alpha]_D^{20}$ 4 (c 0.0006 CHCl₃); UV (c 0.0006, MeOH) λ_{max} 200, 230, 251 nm.



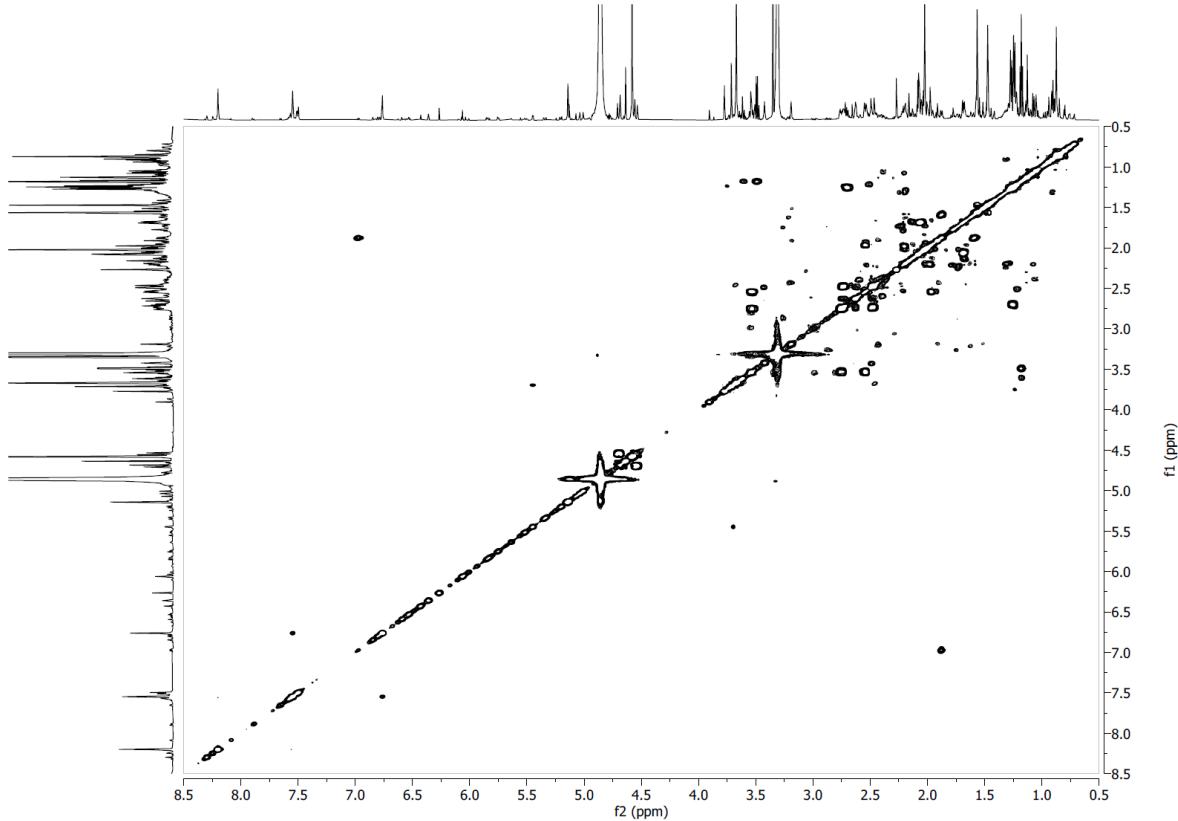
Chemical Formula: C₃₅H₄₂O₁₄

Exact Mass: 686.26

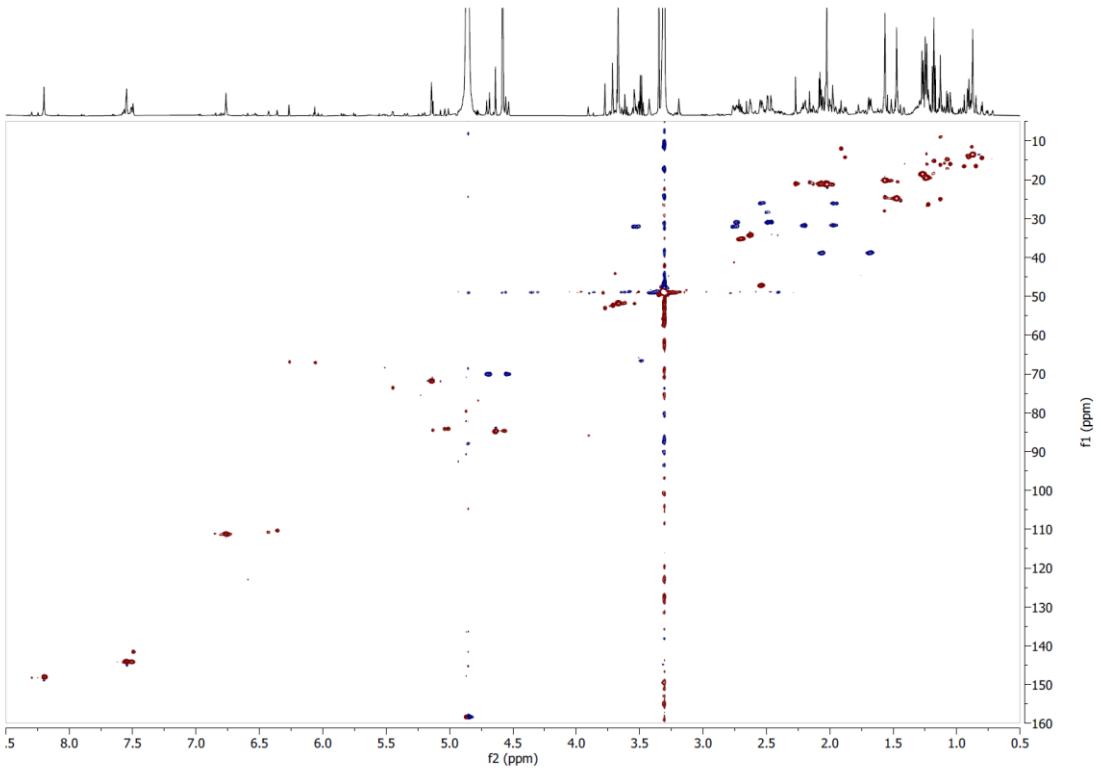
¹H NMR (CD₃OD, 600 MHz) δ 0.87 (3H, s, H₃-28), 1.24 (3H, d, J = 7.2 Hz, H₃-30d), 1.27 (3H, d, J = 6.7 Hz, H₃-30c), 1.47 (3H, s, H₃-18), 1.57 (3H, s, H₃-34), 1.69 (1H, d, J = 10.7 Hz, H-29''), 1.98 (2H, m, H-11'', H-12''), 2.02 (3H, s, H₃-3b), 2.06 (1H, d, J = 10.7 Hz, H-29'), 2.20 (1H, m, H-12'), 2.48 (1H, dd, J = 16.9, 3.2 Hz, H-6''), 2.54 (2H, m, H-11', H-14), 2.63 (1H, m, H-5), 1.70 (1H, m, H-30b), 2.73 (1H, m, H-6'), 2.75 (1H, m, H-15''), 3.67 (3H, s, 16-OCH₃), 4.55 (1H, d, J = 13.6 Hz, H-19''), 4.64 (1H, s, H-3), 4.70 (1H, d, J = 13.6 Hz, H-19'), 5.14 (1H, s, H-30), 6.76 (1H, d, J = 2.0 Hz, H-22), 7.55 (1H, d, J = 2.0 Hz, H-23), 8.20 (1H, s, H-21); ¹³C NMR (CD₃OD, 151 MHz) δ 13.6 (CH₃-28), 18.6 (CH₃-30c), 19.5 (CH₃-30d), 20.2 (CH₃-34), 21.3 (CH₃-3b), 24.8 (CH₃-18), 26.0 (CH₂-11), 30.9 (CH₂-6), 31.8 (CH₂-12), 32.1 (CH₂-15), 34.3 (CH-5), 35.3 (CH-30b), 38.9 (CH₂-29), 45.8 (C-10), 46.0 (C-4), 47.1 (CH-14), 49.3 (C-13), 51.9 (16-OCH₃), 70.0 (CH₂-19), 71.7 (CH-30), 79.5 (C-2), 84.8 (CH-3), 85.3 (C-9), 86.6 (C-1), 87.8 (C-8), 111.3 (CH-22), 120.0 (C-33), 126.4 (C-20), 144.2 (CH-23), 148.1 (CH-21), 171.8 (C-3a), 174.6 (C-7), 175.2 (C-30a), 176.9 (C-16), 199.7 (C-17). Supplementary Figures S4.2.63-S4.2.67.



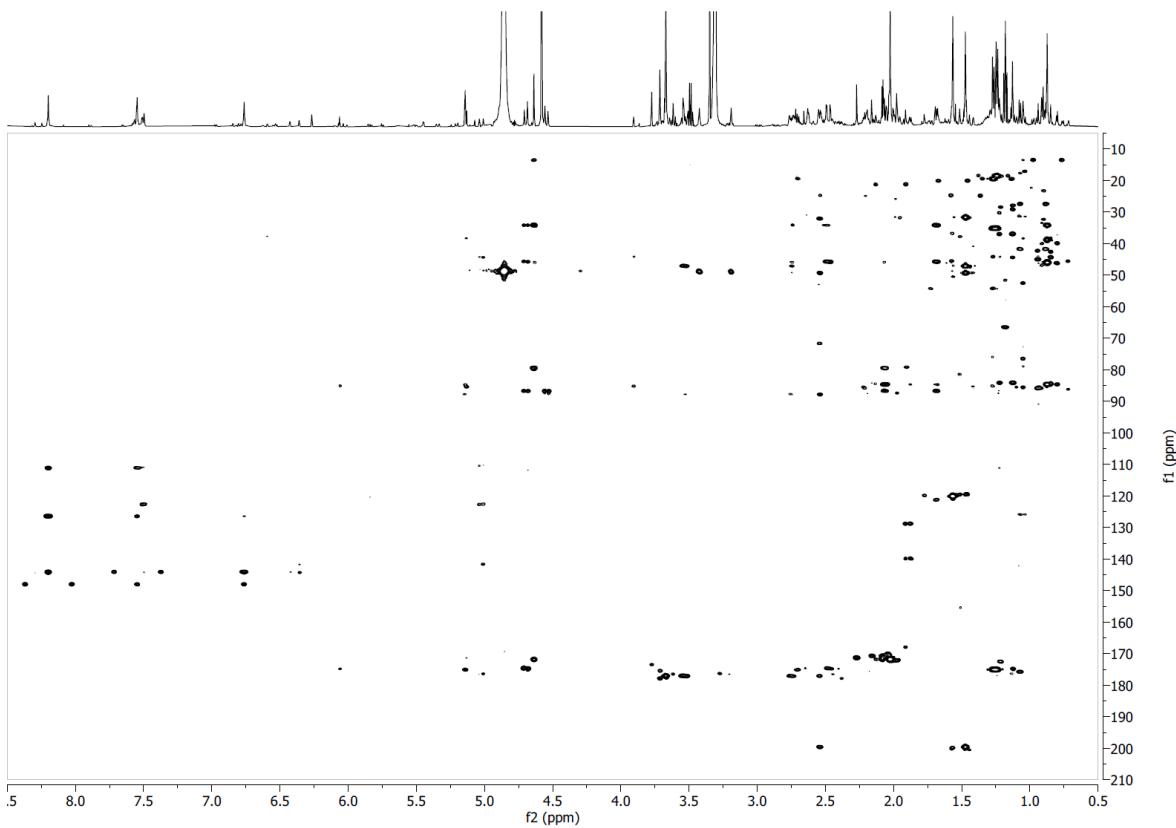
Supplementary Figure S4.2.63. ¹H NMR spectrum of compound 11 in CD₃OD at 600 MHz



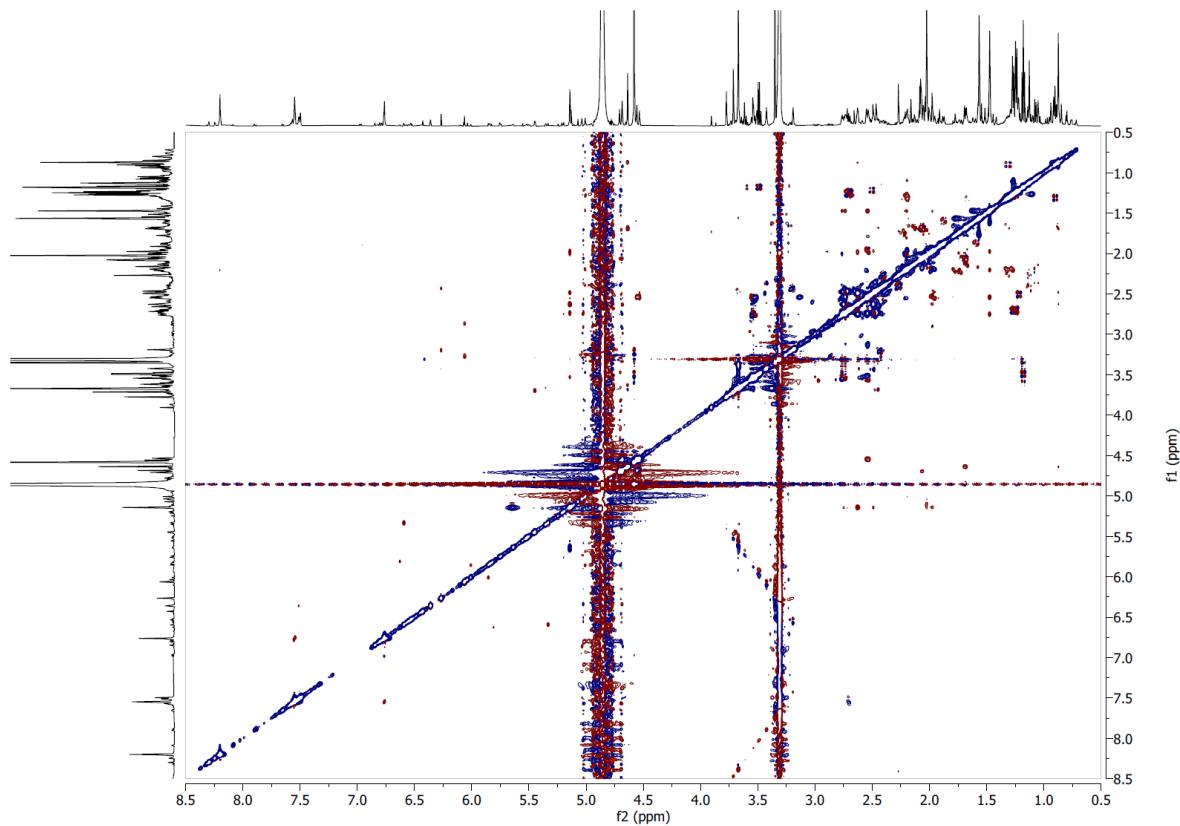
Supplementary Figure S4.2.64. COSY NMR spectrum of compound 11 in CD₃OD



Supplementary Figure S4.2.65. Edited HSQC NMR spectrum of compound **11** in CD_3OD

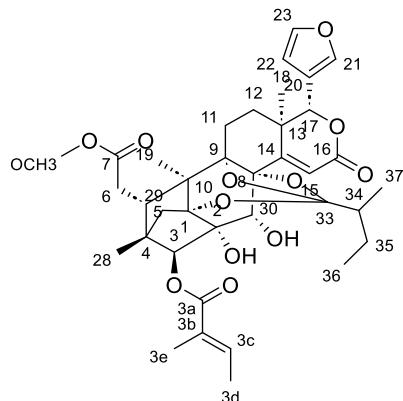


Supplementary Figure S4.2.66. HMBC NMR spectrum of compound **11** in CD_3OD



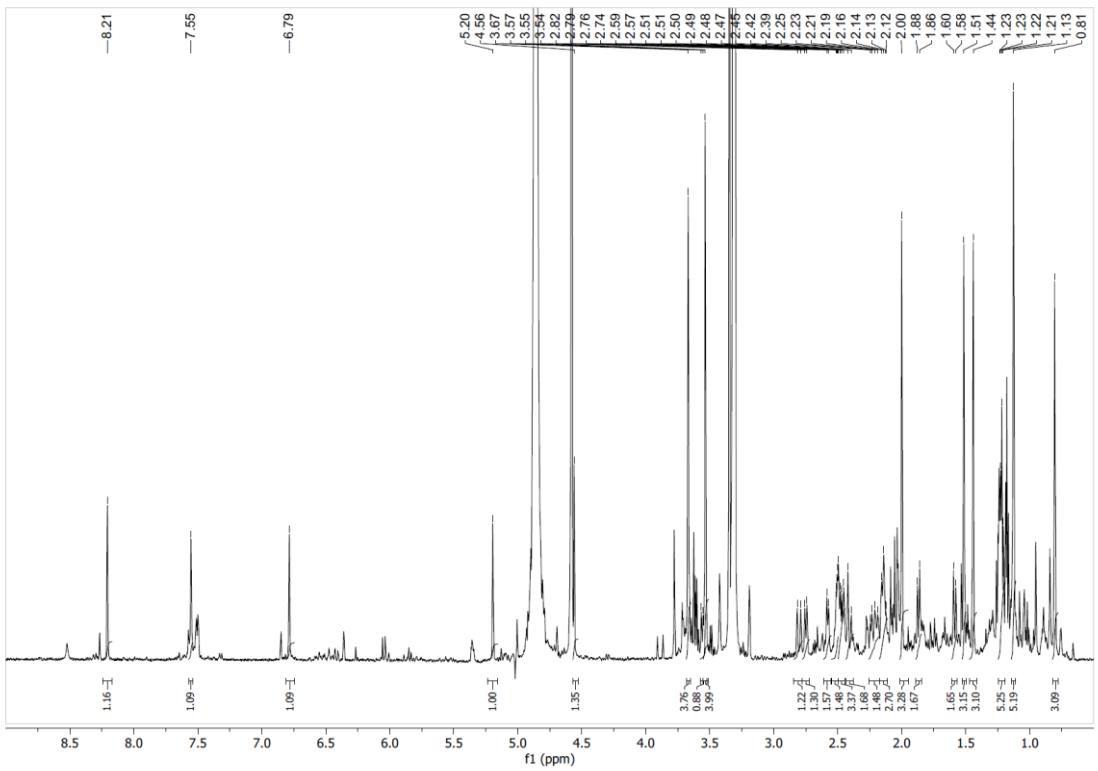
Supplementary Figure S4.2.67. ROESY NMR spectrum of compound **11** in CD_3OD

Compound 12. Amorphous white powder, HRESIMS m/z 689.2807 [M+H]⁺ (calculated for C₃₅H₄₆O₁₄, error 0.54 ppm), 687.2677 [M-H]⁻ (calculated for C₃₅H₄₄O₁₄, error 4.31 ppm); $[\alpha]_D^{20}$ -39 (c 0.0004 CHCl₃); UV (c 0.0004, MeOH) λ_{max} 200, 225, 263 nm.

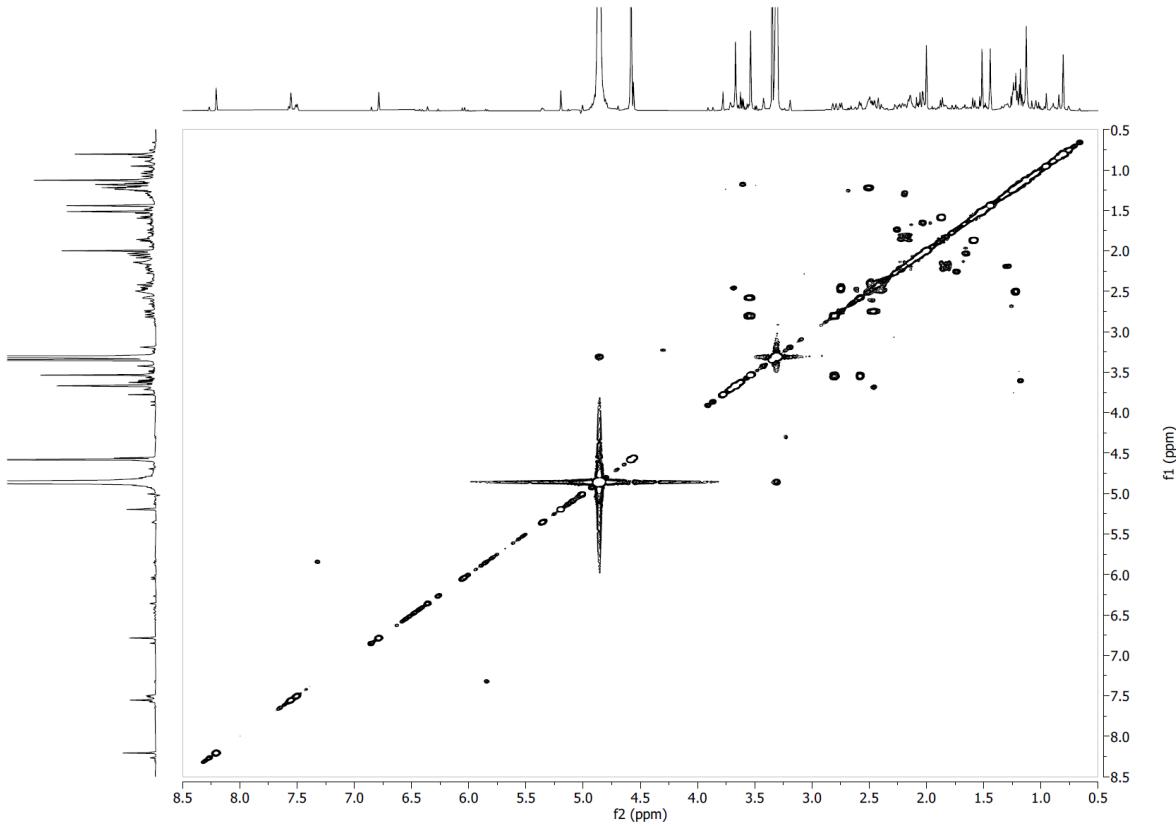


Chemical Formula: C₃₇H₄₆O₁₂
Exact Mass: 682.30

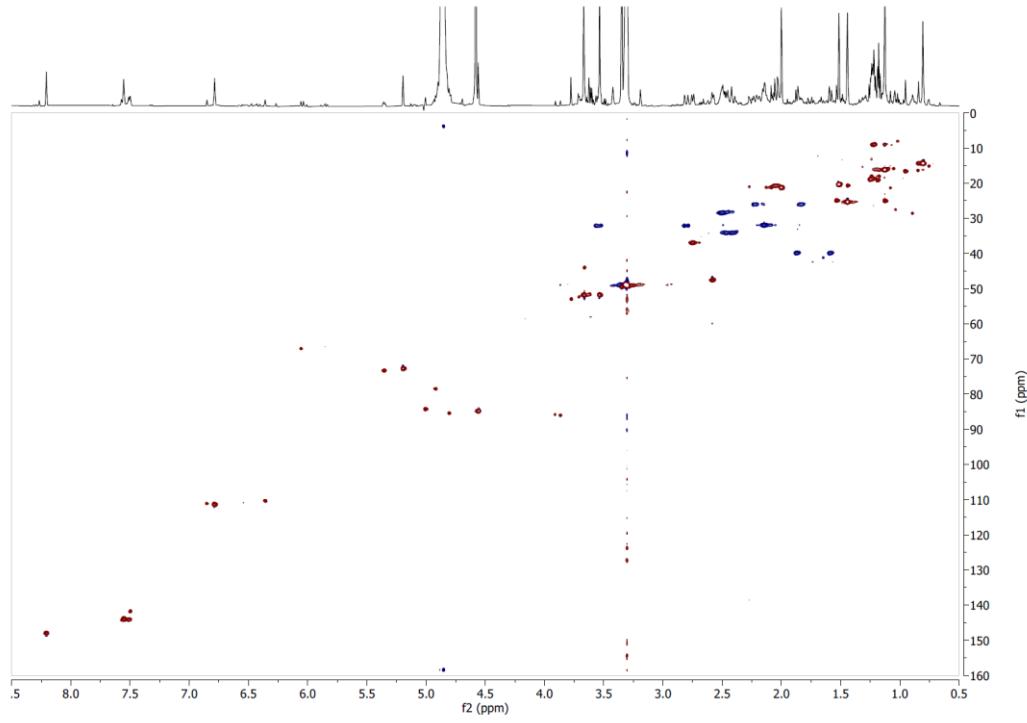
¹H NMR (CD₃OD, 600 MHz) δ 0.81 (3H, s, H₃-28), 1.13 (3H, s, H₃-19), 1.22 (3H, t, J = 7.7 Hz, H₃-30c), 1.44 (3H, s, H₃-18), 1.51 (3H, s, H₃-34), 1.59 (1H, d, J = 10.8 Hz, 29''), 1.83 (1H, m, H-11''), 1.87 (1H, d, J = 10.8 Hz, H-29'), 2.00 (3H, s, H₃-3b), 2.14 (2H, m, H₂-12), 2.22 (1H, m, H-11'), 2.41 (1H, d, J = 15.9 Hz, H-6''), 2.47 (1H, t, J = 15.9, 9.9 Hz, H-6'), 2.51 (2H, m, H₂-30b), 2.58 (2H, d, J = 8.4 Hz, H-14), 2.75 (1H, d, J = 9.9 Hz, H-5), 2.80 (1H, d, J = 16.6 Hz, H-15''), 3.54 (3H, s, OCH₃), 3.55 (1H, dd, J = 16.6, 8.4 Hz, H-15'), 3.67 (3H, s, 16-OCH₃), 4.56 (1H, s, H-3), 5.20 (1H, s, H-30), 6.79 (1H, s, H-22), 7.55 (1H, s, H-23), 8.21 (1H, s, H-21); ¹³C NMR (CD₃OD, 151 MHz) δ 9.0 (CH₃-30c), 14.3 (CH₃-28), 16.2 (CH₃-19), 21.3 (CH₃-3b), 25.3 (CH₃-18), 26.0 (CH₂-11), 28.5 (CH₂-30b), 31.9 (CH₂-12), 32.0 (CH₂-15), 34.1 (CH₂-6), 36.9 (CH-5), 39.9 (CH₂-29), 46.0 (C-10), 46.4 (C-4), 47.4 (CH-14), 49.4 (C-13), 51.9 (OCH₃, 16-OCH₃), 72.6 (CH-30), 79.3 (C-2), 84.8 (CH-3), 86.9 (C-1), 87.4 (C-8), 87.9 (C-9), 111.3 (CH-22), 126.5 (C-20), 144.1 (CH-23), 148.1 (CH-21), 172.3 (C-3a), 172.5 (C-30a), 174.1 (C-7), 177.4 (C-16), 200.6 (C-17). **Supplementary Figures S4.2.68-S4.2.72.**



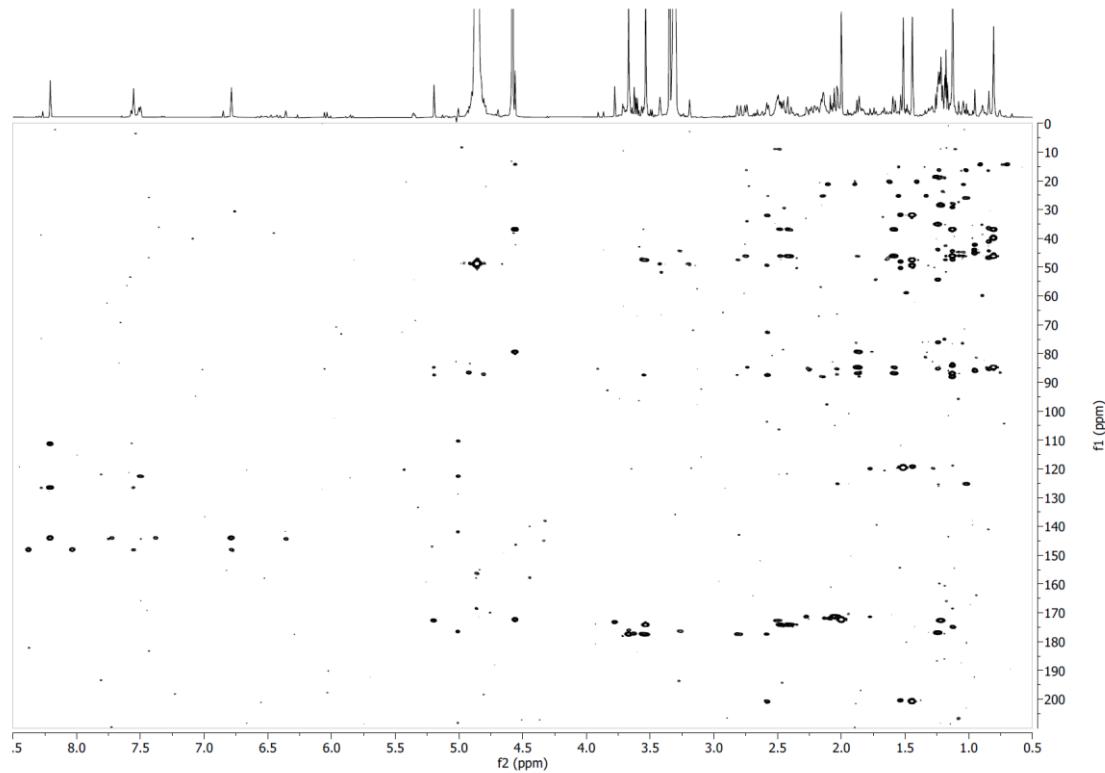
Supplementary Figure S4.2.68. ^1H NMR spectrum of compound **12** in CD_3OD at 600 MHz



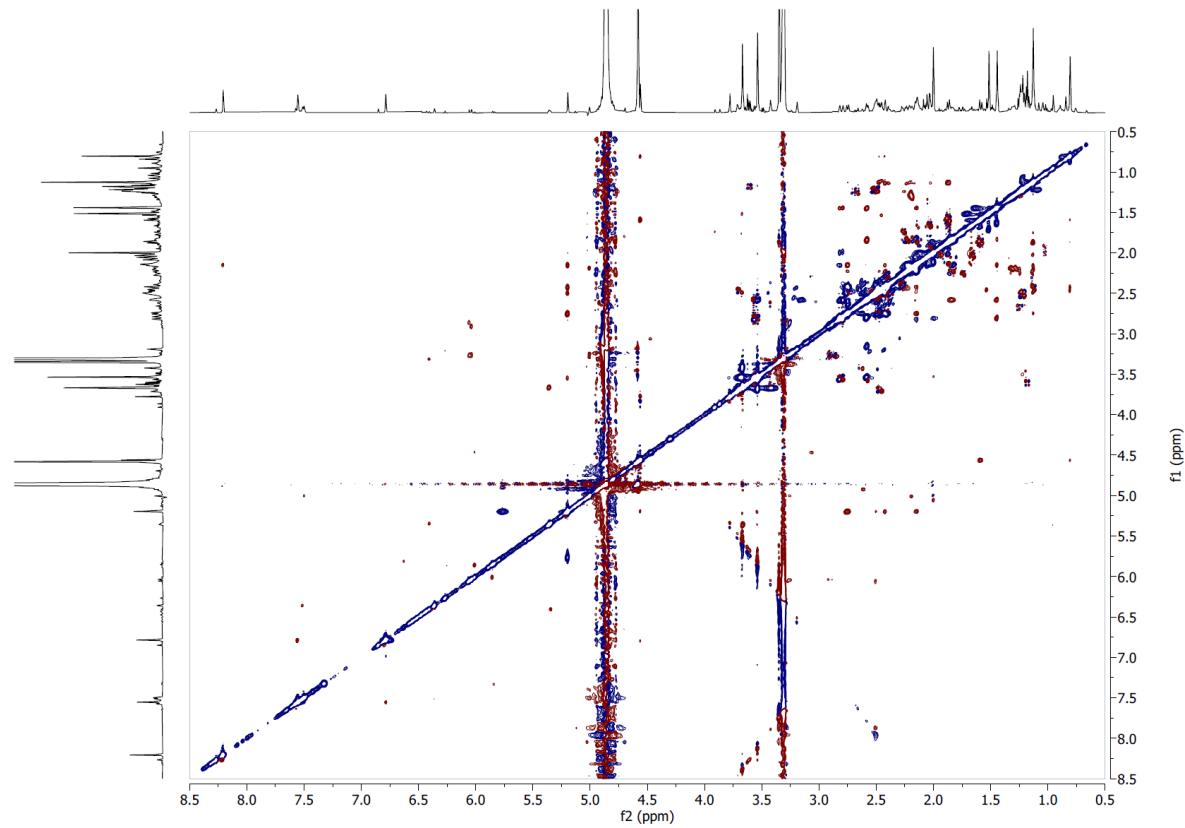
Supplementary Figure S4.2.69. COSY NMR spectrum of compound **12** in CD_3OD



Supplementary Figure S4.2.70. Edited HSQC NMR spectrum of compound **12** in CD_3OD

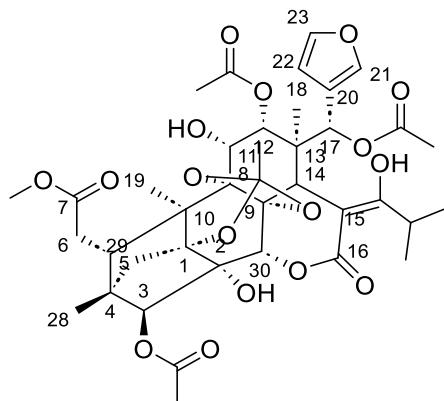


Supplementary Figure S4.2.71. HMBC NMR spectrum of compound **12** in CD_3OD



Supplementary Figure S4.2.72. ROESY NMR spectrum of compound **12** in CD_3OD

Compound 13. Amorphous white powder, HRESIMS m/z 789.2973 [M+H]⁺ (calculated for C₃₉H₄₉O₁₇, error 1.18 ppm), 787.2811 [M-H]⁻ (calculated for C₃₉H₄₇O₁₇, error 0.52 ppm); $[\alpha]_D^{20} -28$ (c 0.0008 CHCl₃); UV (c 0.0008, MeOH) λ_{max} 200, 224, 275 nm.

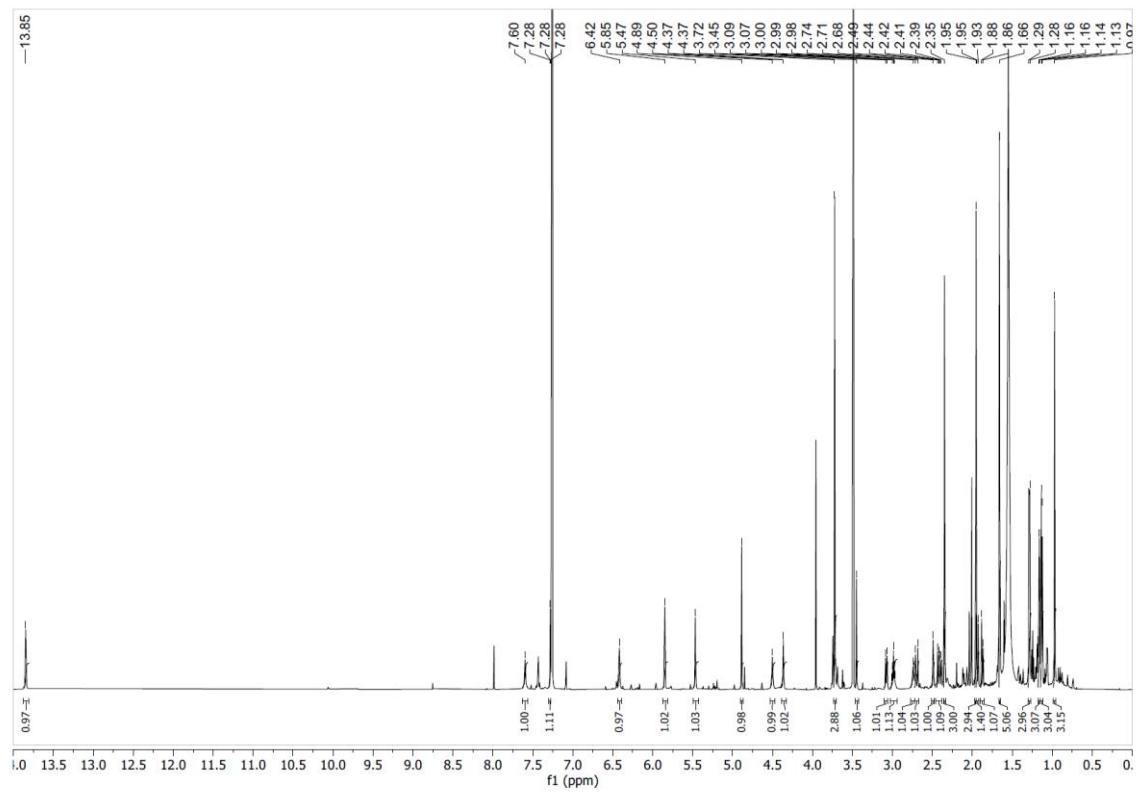


Chemical Formula: C₃₉H₄₈O₁₇

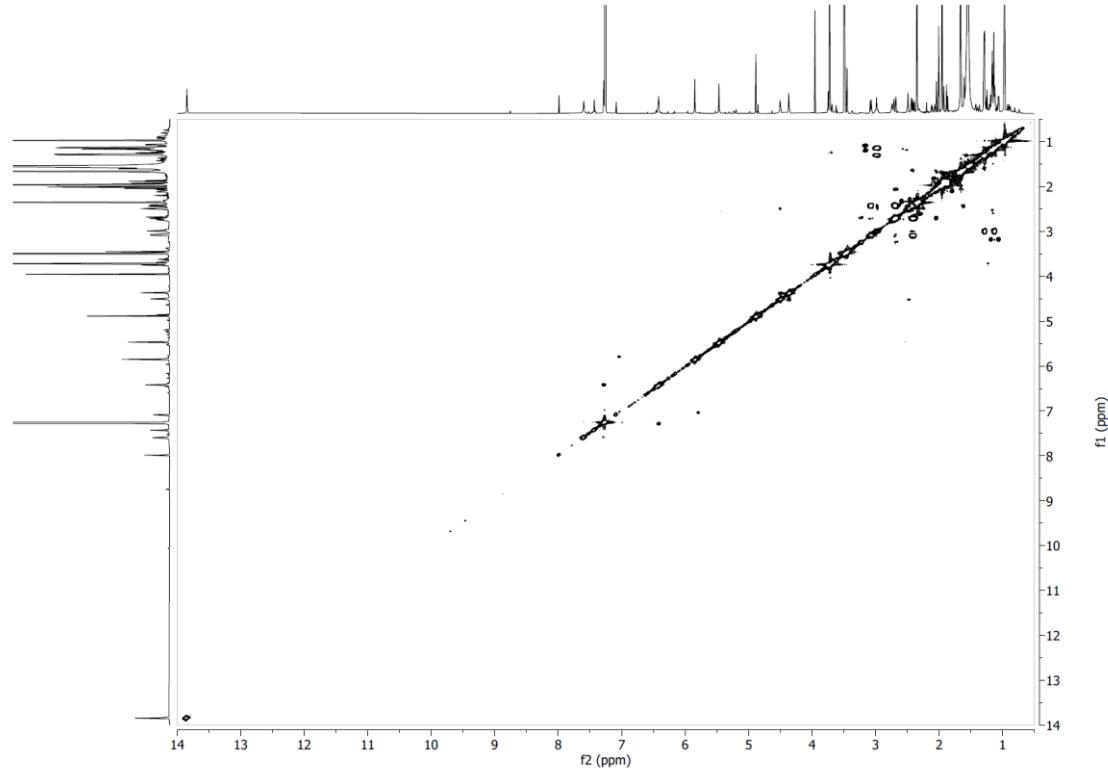
Exact Mass: 788.29

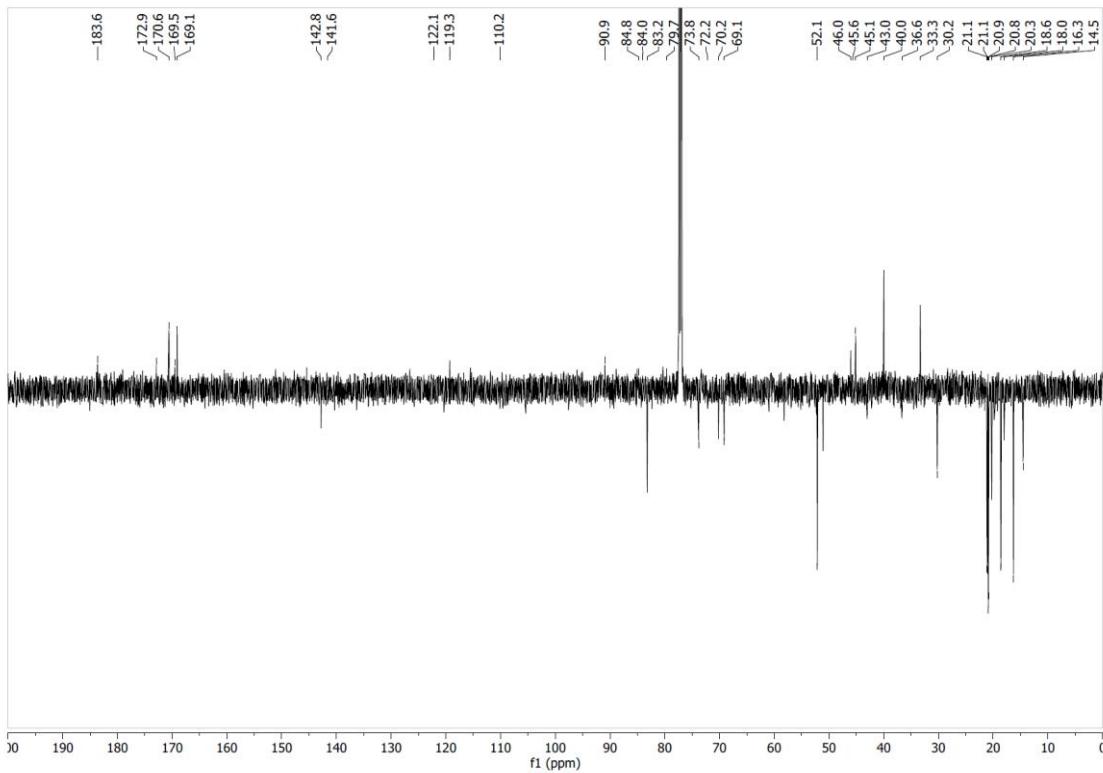
¹H NMR (CDCl₃, 600 MHz) δ 0.97 (3H, s, H₃-28), 1.13 (3H, d, J = 6.7 Hz, H₃-15d), 1.16 (3H, s, H₃-19), 1.29 (3H, d, J = 6.7 Hz, H₃-15c), 1.53 (3H, overlapped, H₃-18), 1.66 (6H, s, H₃-12b, H₃-34), 1.87 (1H, d, J = 11.1 Hz, H-29''), 1.94 (1H, d, J = 11.1 Hz, H-29'), 1.95 (3H, s, H₃-17b), 2.35 (3H, s, H₃-3b), 2.41 (1H, dd, J = 17.5, 10.8 Hz, H-6''), 2.49 (1H, s, OH-11), 2.70 (1H, d, J = 17.5 Hz, H-6'), 2.74 (1H, s, OH-2), 2.99 (1H, hept, J = 6.7 Hz, H-15b), 3.08 (1H, d, J = 10.8 Hz, H-5), 3.45 (1H, s, H-14), 3.72 (3H, s, OCH₃), 4.37 (1H, s, H-11), 4.50 (1H, s, H-12), 4.89 (1H, s, H-3), 5.47 (1H, s, H-30), 5.85 (1H, s, H-17), 6.42 (1H, s, H-22), 7.28 (1H, t, J = 1.7 Hz, H-23), 7.60 (1H, s, H-21), 13.85 (1H, s, OH-15a); ¹³C NMR (CDCl₃, 151 MHz) δ 14.5 (CH₃-28), 16.3 (CH₃-19), 18.0 (CH₃-18), 18.6 (CH₃-15c), 20.3 (CH₃-34), 20.8 (CH₃-15d), 20.9 (CH₃-17b), 21.1 (CH₃-3b), 21.1 (CH₃-12b), 30.2 (CH-15b), 33.3 (CH₂-6), 36.6 (CH-5), 40.0 (CH₂-29), 43.0 (CH-14), 45.1 (C-13), 45.6 (C-10), 46.0 (C-4), 52.1 (OCH₃), 69.1 (CH-11), 70.2 (CH-17), 72.2 (CH-12), 73.8 (CH-30), 79.7 (C-8), 83.2 (CH-3), 84.0 (C-9), 84.8 (C-1), 90.9 (C-15), 110.2 (CH-22), 119.3 (C-33), 122.1 (C-20), 141.6 (CH-21), 142.8 (CH-23), 169.1 (C-17a), 169.5 (C-12a), 170.6 (C-16), 172.9 (C-7), 183.6 (C-15a).

Supplementary Figures S4.2.73-S4.2.78.

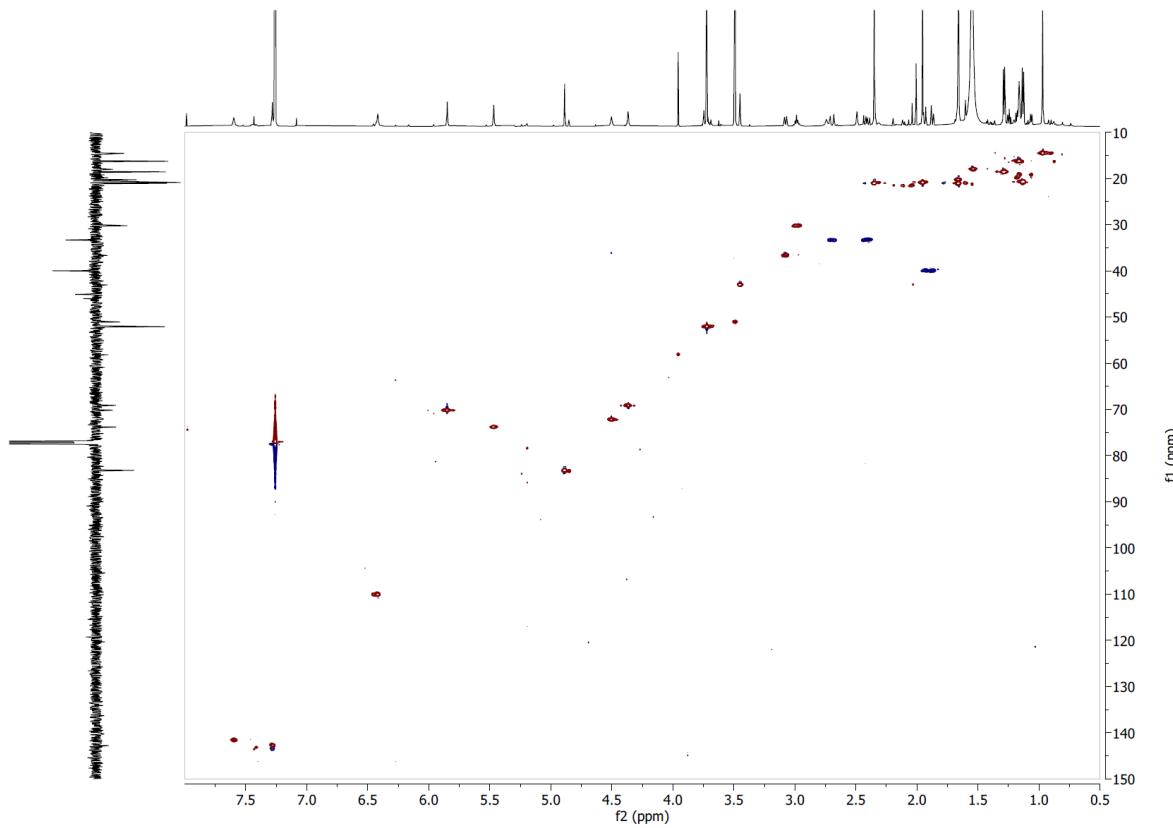


Supplementary Figure S4.2.73. ^1H NMR spectrum of compound **13** in CDCl_3 at 600 MHz

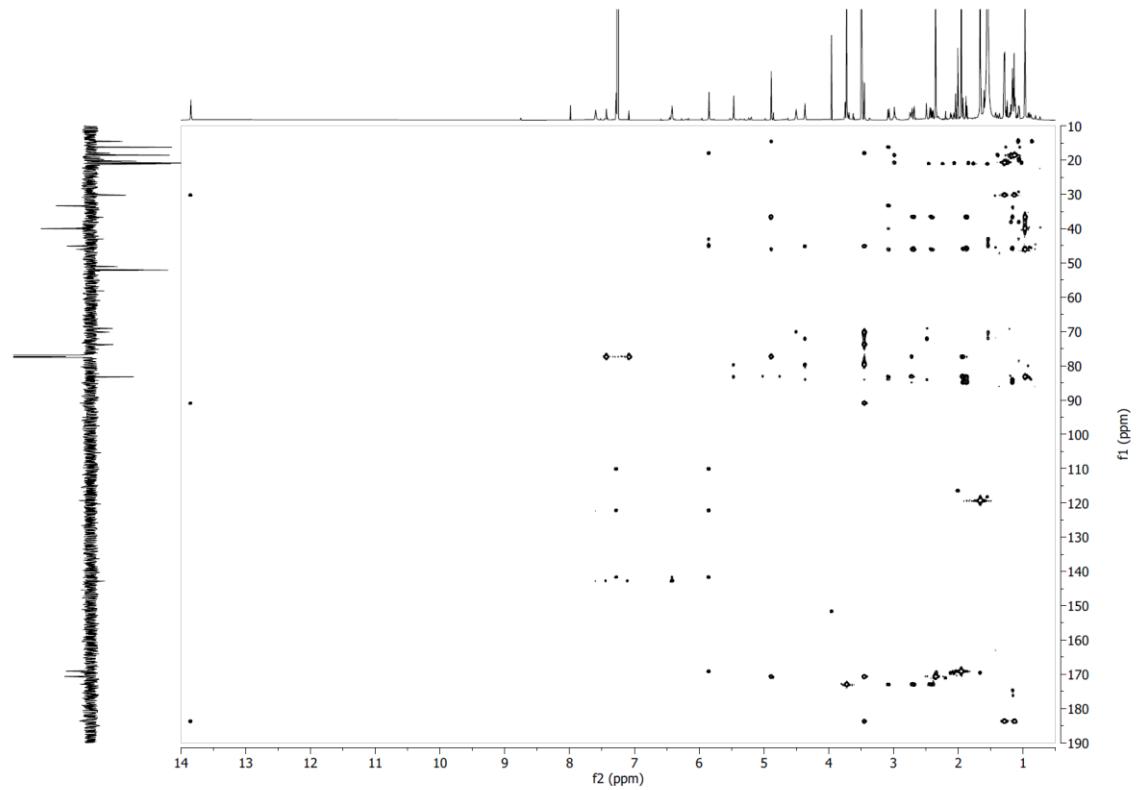




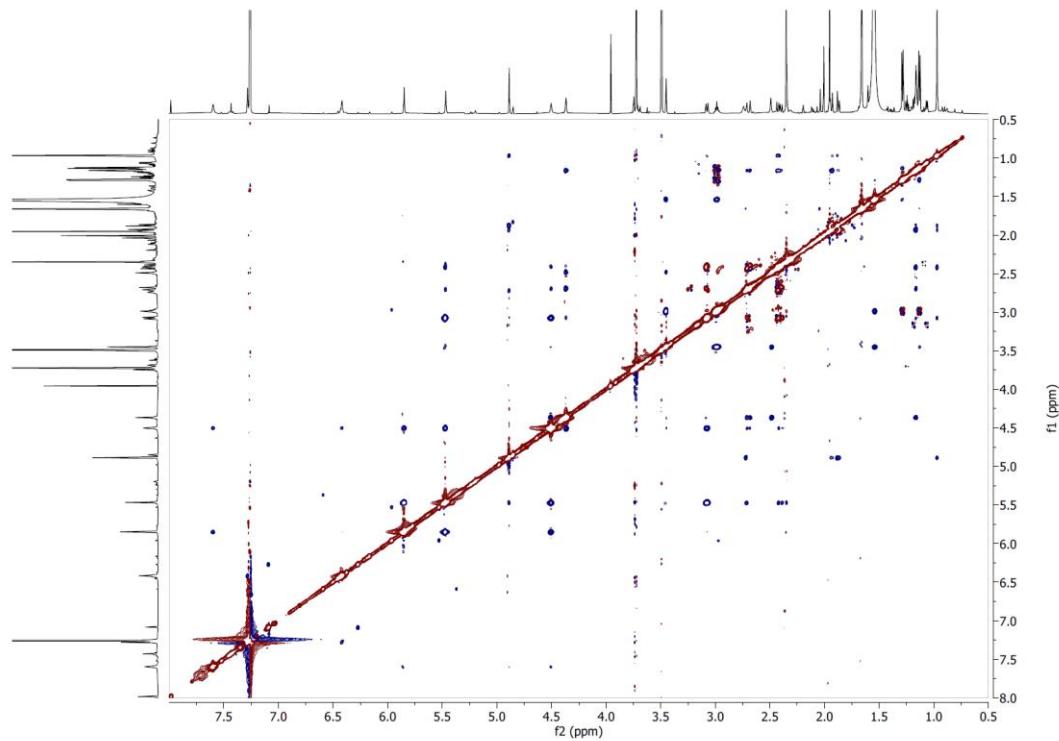
Supplementary Figure S4.2.75. ^{13}C -DEPTQ NMR spectrum of compound **13** in CDCl_3 at 151 MHz



Supplementary Figure S4.2.76. Edited HSQC NMR spectrum of compound **13** in CDCl_3

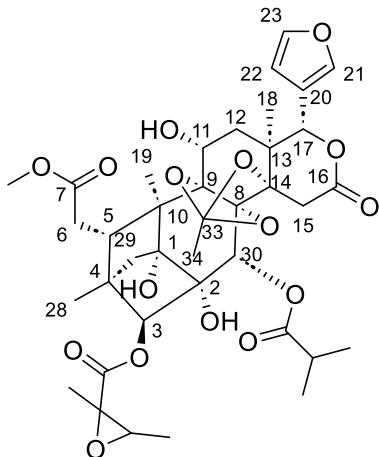


Supplementary Figure S4.2.77. HMBC NMR spectrum of compound **13** in CDCl_3



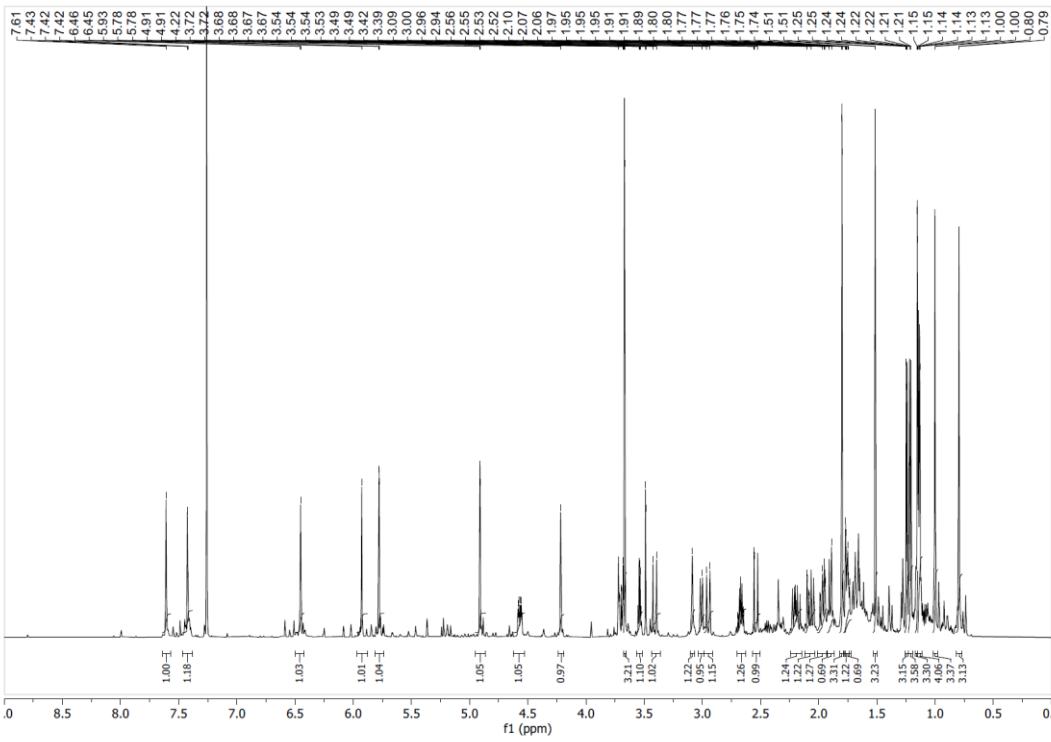
Supplementary Figure S4.2.78. ROESY NMR spectrum of compound **13** in CDCl_3

Compound 14. Amorphous white powder, HRESIMS m/z 761.3014 [M+H]⁺ (calculated for C₃₈H₄₉O₁₆, error -0.08 ppm), 759.2868 [M-H]⁻ (calculated for C₃₈H₄₇O₁₆, error 1.53 ppm); $[\alpha]_D^{20}$ -7 (c 0.005 CHCl₃); UV (c 0.005, MeOH) λ_{max} 200, 226, 274 nm.

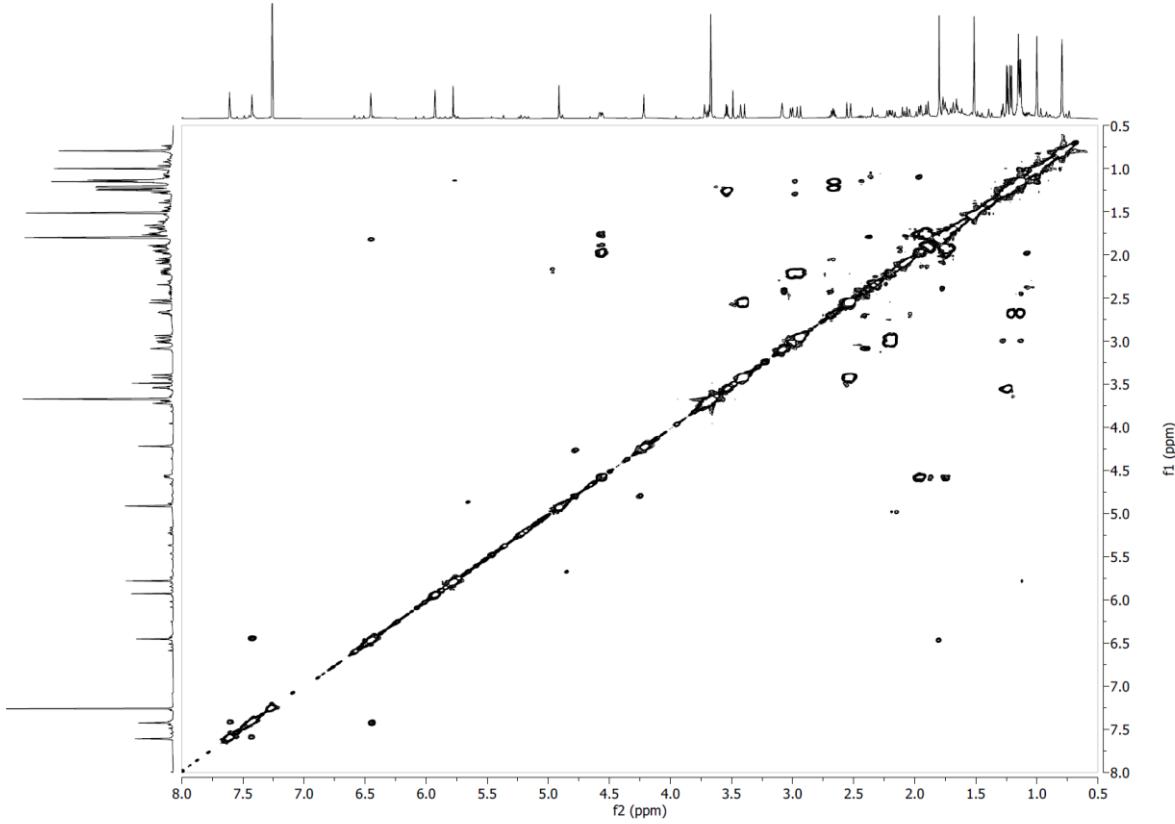


Chemical Formula: C₃₈H₄₈O₁₆
Exact Mass: 760.29

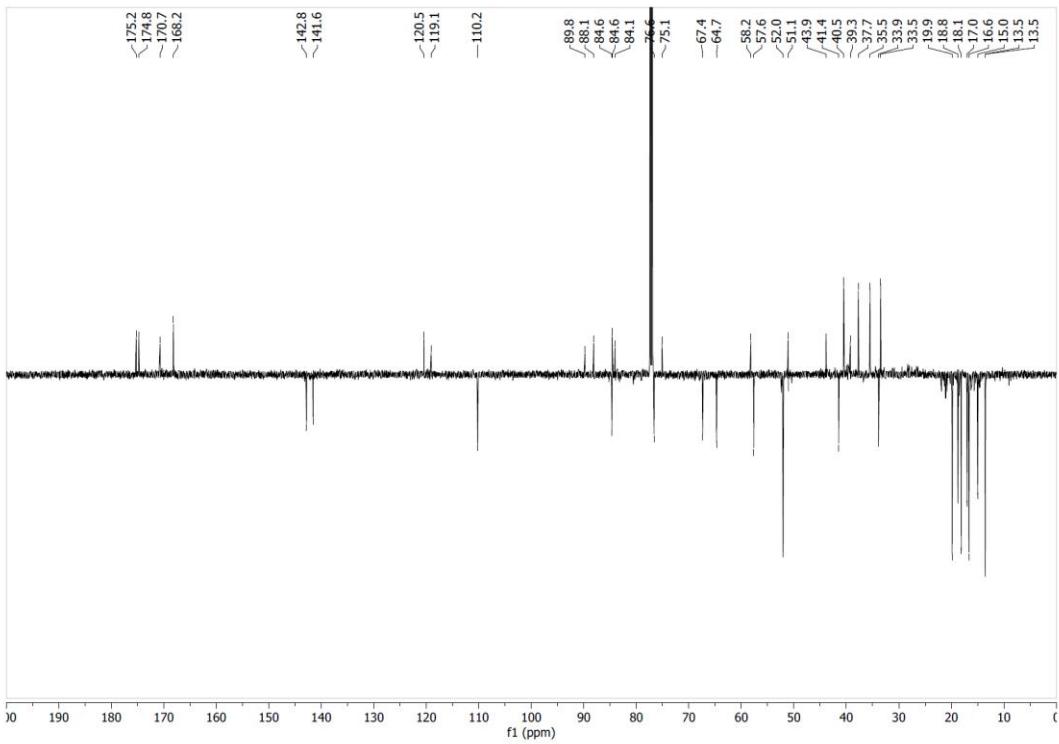
¹H NMR (CDCl₃, 600 MHz) δ 0.79 (3H, s, H₃-28), 1.00 (3H, s, H₃-18), 1.14 (3H, d, J = 7.0 Hz, H₃-30d), 1.15 (3H, s, H₃-19), 1.21 (3H, d, J = 7.0 Hz, H₃-30c), 1.24 (3H, d, J = 5.3 Hz, H₃-3d), 1.51 (3H, s, H₃-3e), 1.75 (1H, dd, J = 13.7, 5.0 Hz, H-12b), 1.76 (1H, d, J = 11.0 Hz, H-29¹¹), 1.80 (3H, s, H₃-34), 1.90 (1H, d, J = 11.0 Hz, H-29¹), 1.97 (1H, t, J = 13.7, 11.9 Hz, H-12a), 2.20 (1H, dd, J = 16.4, 11.6 Hz, H-6¹¹), 2.54 (1H, d, J = 18.8 Hz, H-15a), 2.67 (1H, hept, J = 7.0 Hz, H-30b), 2.95 (1H, d, J = 16.5 Hz, H-6¹), 3.01 (1H, d, J = 11.6 Hz, H-5), 3.09 (1H, s, 2-OH), 3.41 (1H, d, J = 18.8 Hz, H-15b), 3.54 (1H, q, J = 5.3 Hz, H-3c), 3.67 (3H, s, OCH₃), 4.22 (1H, s, 1-OH), 4.57 (1H, dd, J = 11.9, 5.0 Hz, H-11), 4.91 (1H, s, H-3), 5.78 (1H, s, H-30), 5.93 (1H, s, H-17), 6.45 (1H, d, J = 2.0 Hz, H-22), 7.42 (1H, d, J = 2.0 Hz, H-23), 7.61 (1H, s, H-21); ¹³C NMR (CDCl₃, 151 MHz) δ 13.5 (CH₃-3d), 13.5 (CH₃-3e), 15.0 (CH₃-28), 16.6 (CH₃-34), 17.0 (CH₃-19), 18.1 (CH₃-30d), 18.8 (CH₃-18), 19.9 (CH₃-30c), 33.5 (CH₂-6), 33.9 (CH-30b), 35.5 (CH₂-12), 37.7 (CH₂-15), 39.3 (C-13), 40.5 (CH₂-29), 41.4 (CH-5), 43.9 (C-4), 51.1 (C-10), 52.0 (OCH₃), 57.6 (CH-3c), 58.2 (C-3b), 64.7 (CH-30), 67.4 (CH-11), 75.1 (C-2), 76.6 (CH-17), 84.1 (C-14), 84.6 (C-9), 84.6 (CH-3), 88.1 (C-1), 89.8 (C-8), 110.2 (CH-22), 119.1 (C-33), 120.5 (C-20), 141.6 (CH-21), 142.8 (CH-23), 168.2 (C-16), 170.7 (C-3a), 174.8 (C-30a), 175.2 (C-7). Supplementary Figures S4.2.79-S4.2.84.



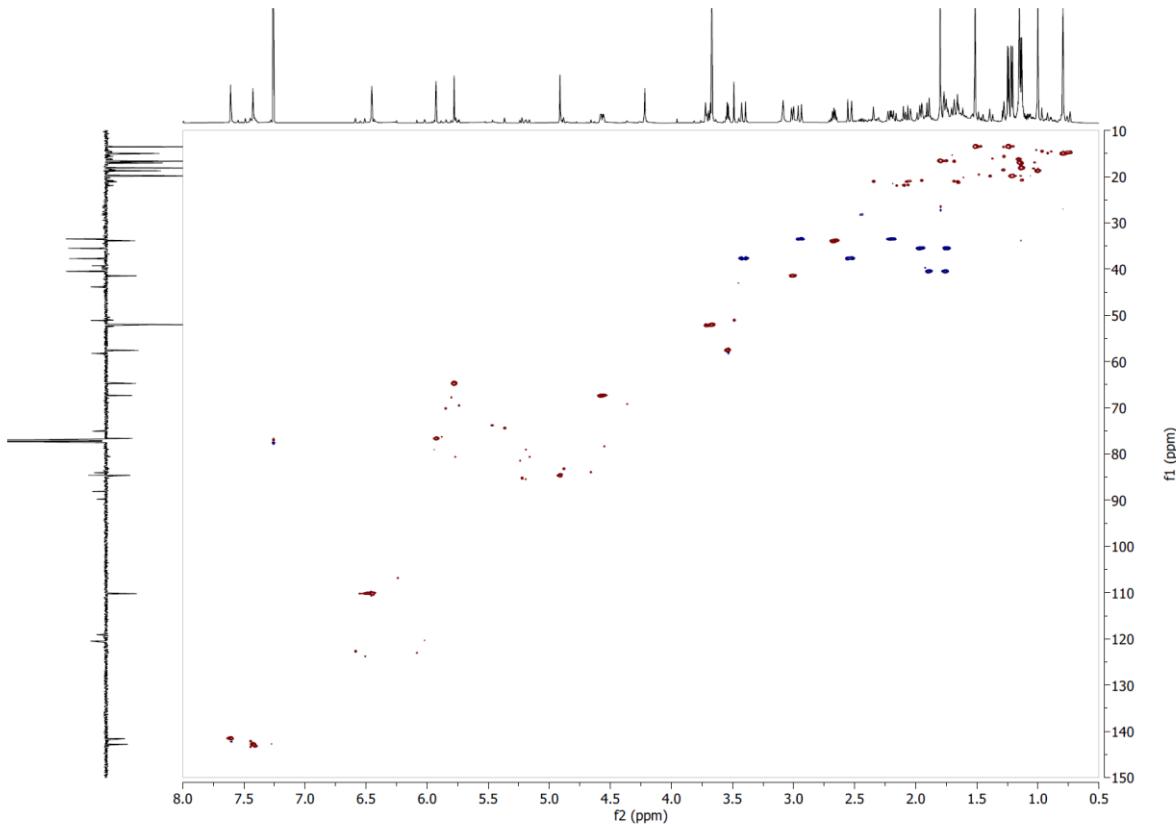
Supplementary Figure S4.2.79. ^1H NMR spectrum of compound **14** in CDCl_3 at 600 MHz



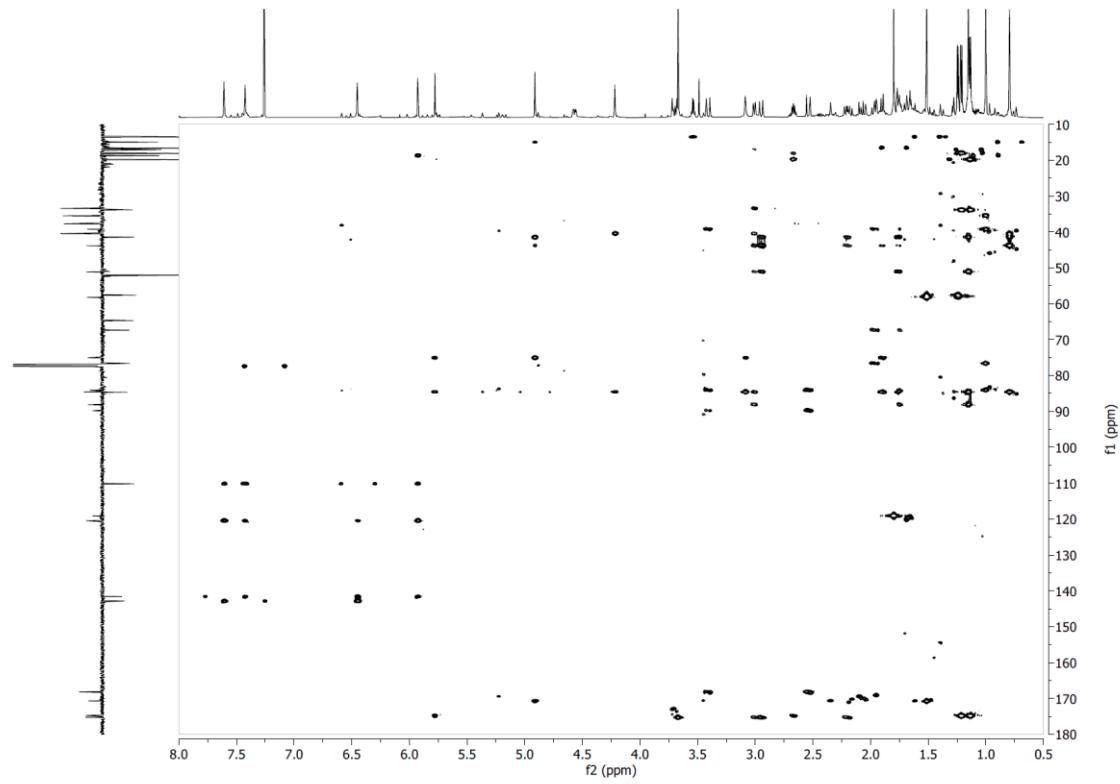
Supplementary Figure S4.2.80. COSY NMR spectrum of compound **14** in CDCl_3



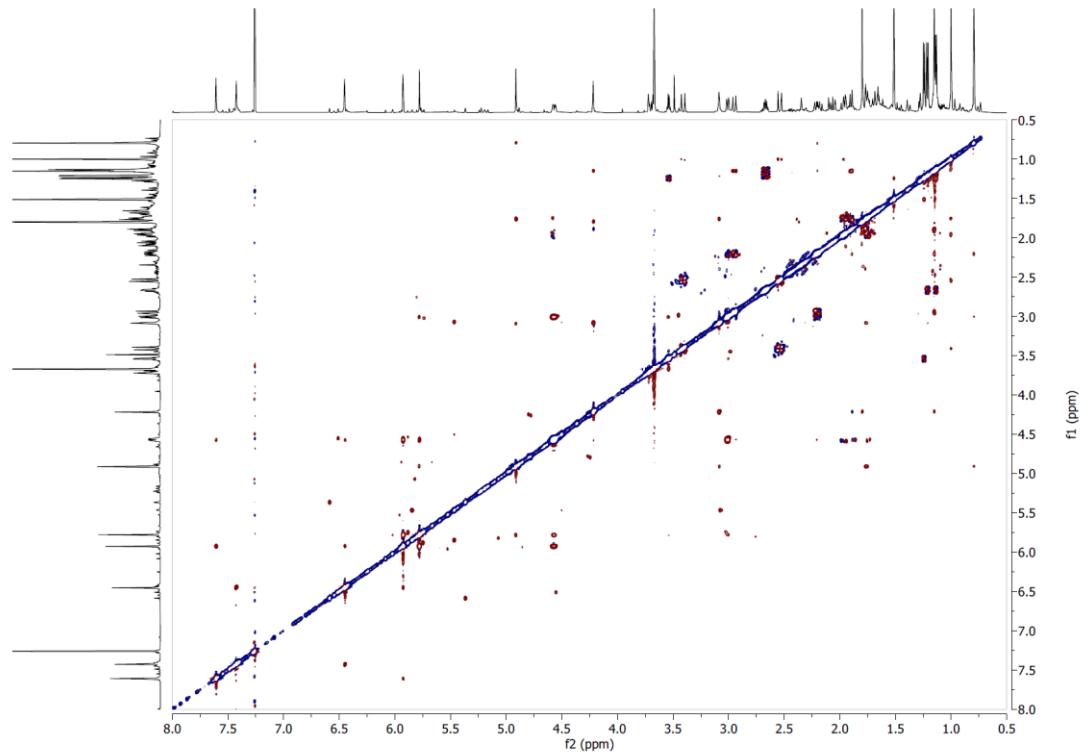
Supplementary Figure S4.2.81. ^{13}C -DEPTQ NMR spectrum of compound **14** in CDCl_3 at 151 MHz



Supplementary Figure S4.2.82. Edited HSQC NMR spectrum of compound **14** in CDCl_3

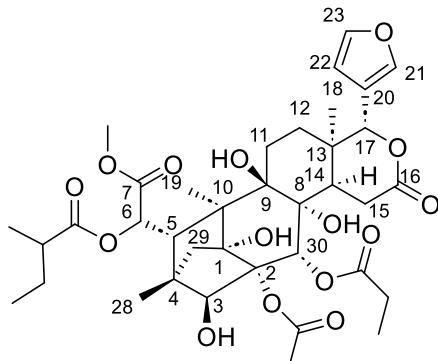


Supplementary Figure S4.2.83. HMBC NMR spectrum of compound **14** in CDCl_3



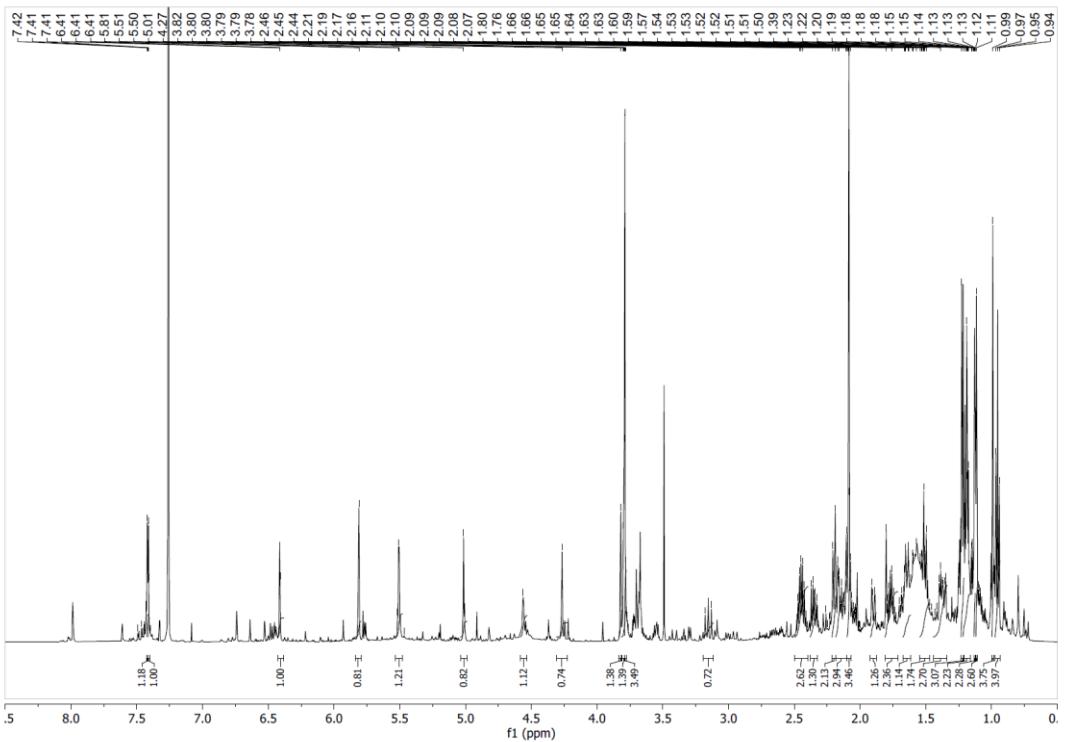
Supplementary Figure S4.2.84. ROESY NMR spectrum of compound **14** in CDCl_3

Compound 15. Amorphous white powder, HRESIMS m/z 757.3053 [M+Na]⁺ (calculated for C₃₇H₅₀O₁₅Na, error 1.54 ppm), 733.3070 [M-H]⁻ (calculated for C₃₇H₄₉O₁₅, error 0.56 ppm); $[\alpha]_D^{20}$ -7 (c 0.002CHCl₃); UV (c 0.002, MeOH) λ_{max} 200, 241, 285 nm.

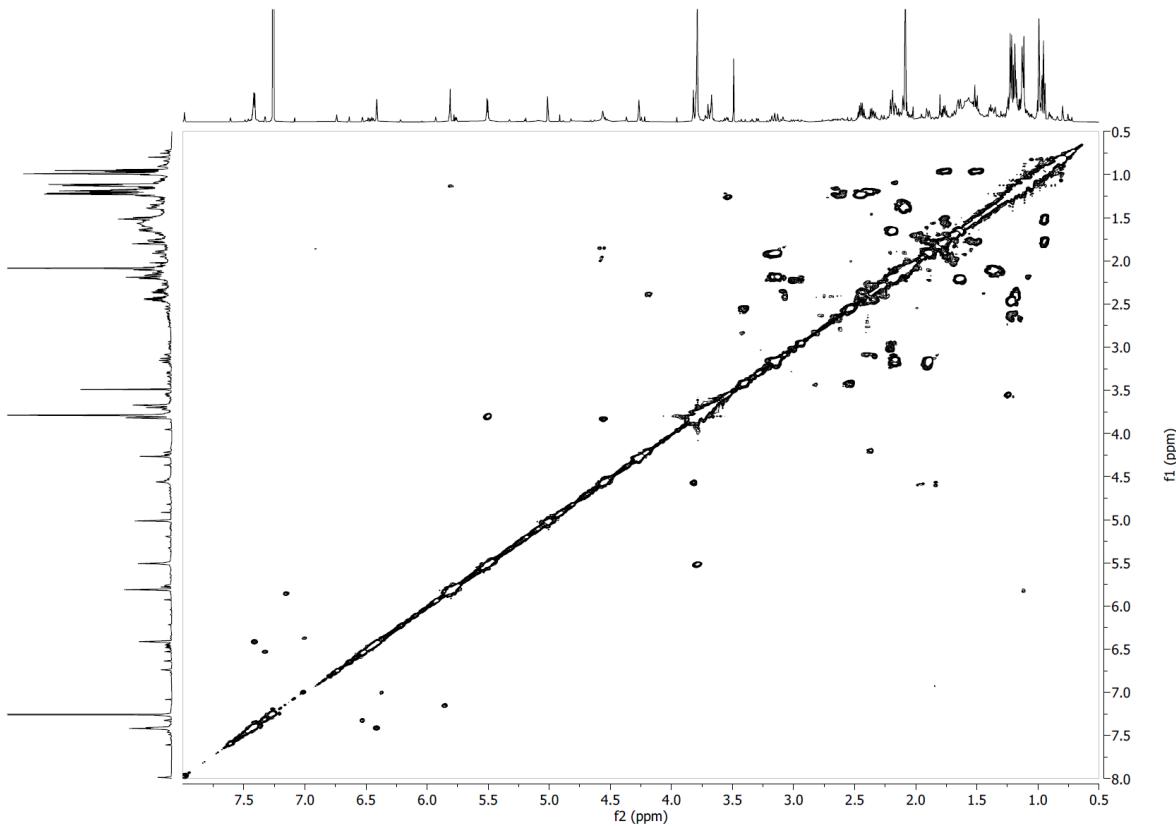


Chemical Formula: C₃₇H₅₀O₁₅
Exact Mass: 734.31

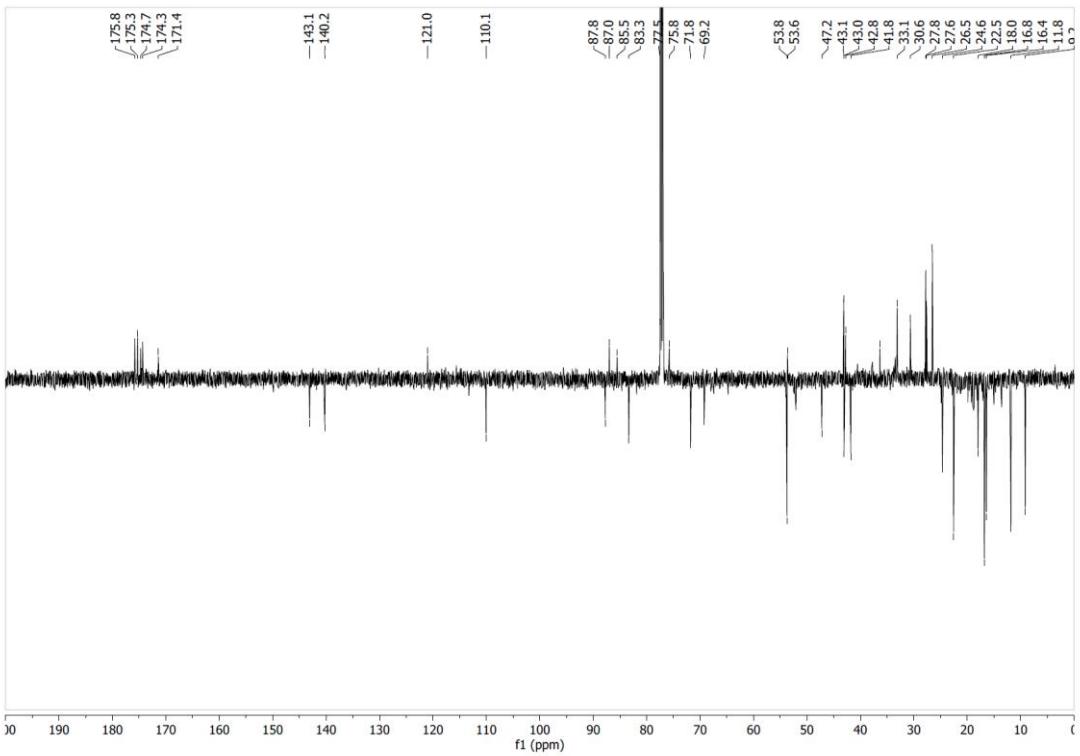
¹H NMR (CDCl₃, 600 MHz) δ 0.95 (3H, t, J = 7.4 Hz, H₃-6d), 0.99 (3H, s, H₃-28), 1.11 (3H, s, H₃-18), 1.13 (3H, s, H₃-19), 1.19 (3H, t, J = 7.6 Hz, H₃-30c), 1.22 (3H, d, J = 7.1 Hz, H₃-6e), 1.35 (1H, m, H-11α)[LQG1] [LM2], 1.39 (1H, m, H-12α), 1.51 (1H, m, H-6c¹), 1.64 (1H, d, J = 10.7 Hz, H-29pro-R), 1.77 (1H, m, H-6c¹), 1.90 (1H, dd, J = 13.4, 3.2 Hz, H-14), 2.09 (3H, s, H₃-2b), 2.11 (1H, m, H-12β), 2.13 (1H, m, H-11β), 2.17 (1H, m, H-15α), 2.20 (1H, d, J = 10.7 Hz, H-29pro-S), 2.35 (1H, m, H-30b¹), 2.44 (2H, m, H-6b, H-30b¹), 3.15 (1H, t, J = 15.1, 13.4 Hz, H-15β), 3.79 (3H, s, OCH₃), 3.80 (1H, d, J = 4.1 Hz, H-5), 3.82 (1H, s, H-3), 4.27 (1H, s, OH-9), 4.56 (1H, s, OH-3), 5.01 (1H, s, H-17), 5.51 (1H, d, J = 4.1 Hz, H-6), 5.81 (1H, s, H-30), 6.41 (1H, t, J = 1.7, 0.9 Hz, H-22), 7.41 (1H, t, J = 1.7 Hz, H-23), 7.42 (1H, d, J = 0.9 Hz, H-21); ¹³C NMR (CDCl₃, 151 MHz) δ 9.2 (CH₃-30c), 11.8 (CH₃-6d), 16.4 (CH₃-28), 16.8 (CH₃-6e), 18.0 (CH₃-19), 22.5 (CH₃-2b), 24.6 (CH₃-18), 26.5 (CH₂-6c), 27.6 (CH₂-11), 27.8 (CH₂-30b), 30.6 (CH₂-12), 33.1 (CH₂-15), 36.36.33 (C-13), 41.8 (CH-6b), 42.8 (C-4), 43.0 (CH-5), 43.1 (CH₂-29), 47.2 (CH-14), 53.6 (C-10), 53.8 (OCH₃), 69.2 (CH-30), 71.8 (CH-6), 75.8 (C-9), 77.5 (C-8), 83.3 (CH-17), 85.5 (C-2), 87.0 (C-1), 87.8 (CH-3), 110.1 (CH-22), 121.0 (C-20), 140.2 (CH-21), 143.1 (CH-23), 171.4 (C-2a), 174.3 (C-7), 174.7 (C-16), 175.3 (C-6a), 175.8 (C-30a). **Supplementary Figures S4.2.85-S4.2.90.**



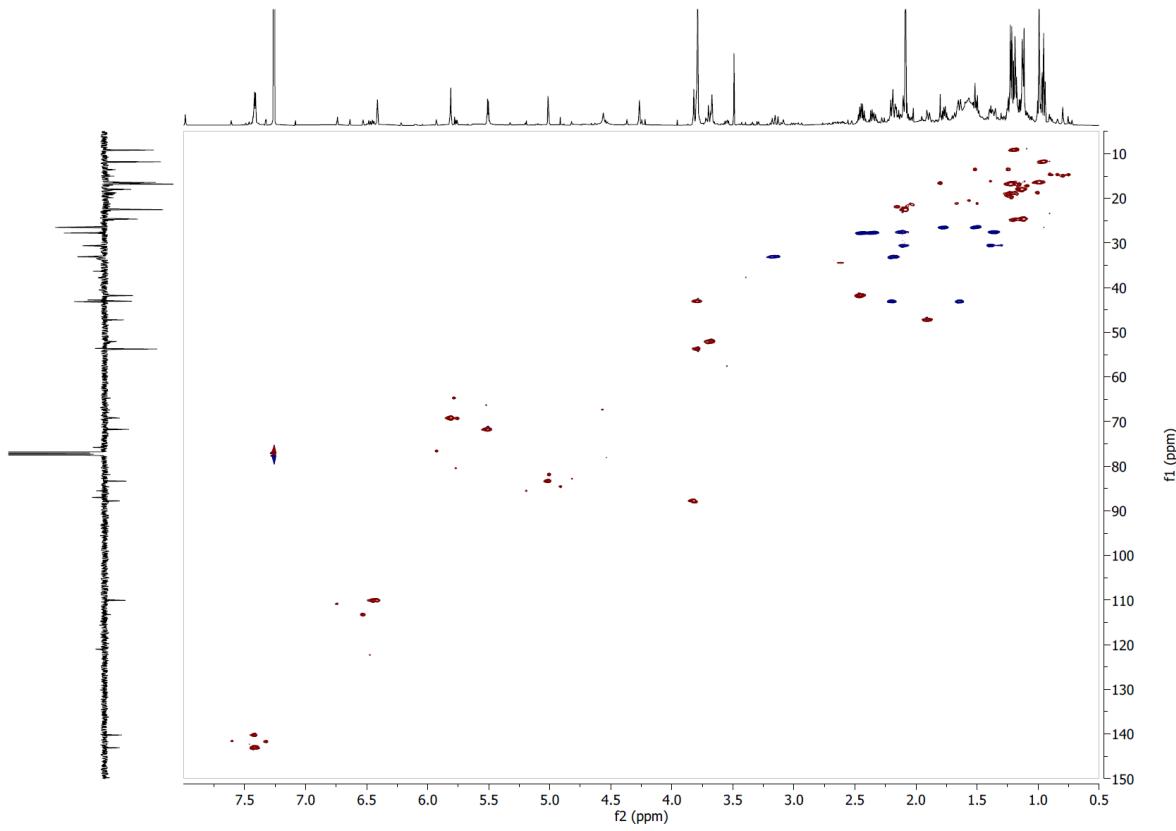
Supplementary Figure S4.2.85. ^1H NMR spectrum of compound **15** in CDCl_3 at 600 MHz



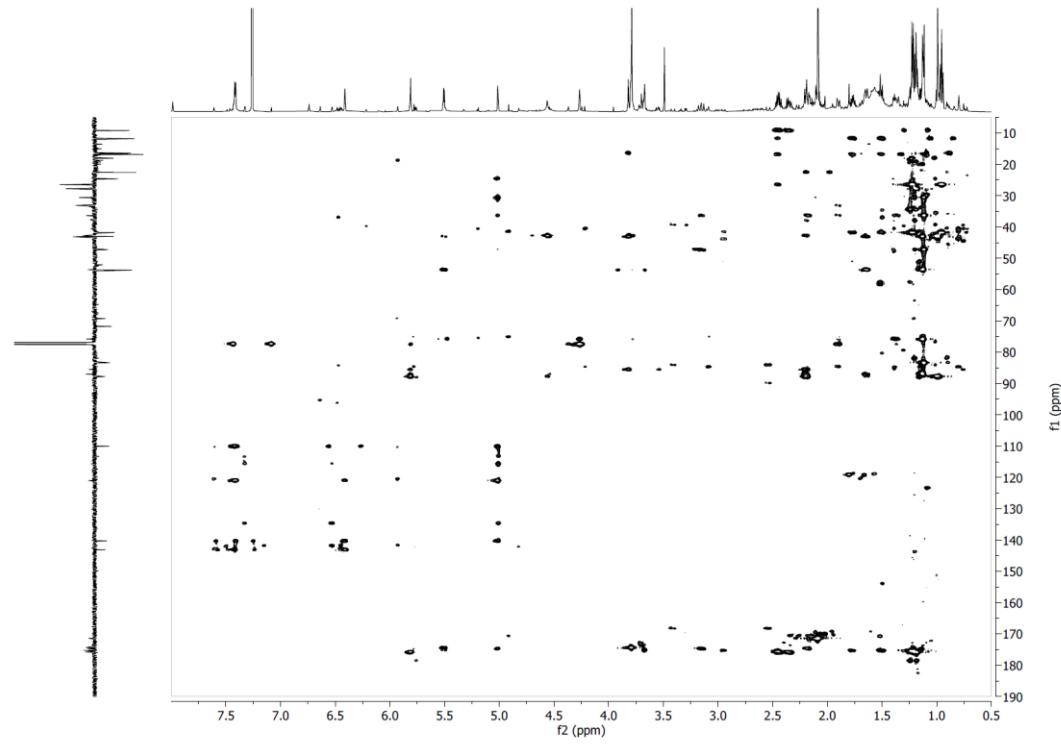
Supplementary Figure S4.2.86. COSY NMR spectrum of compound **15** in CDCl_3



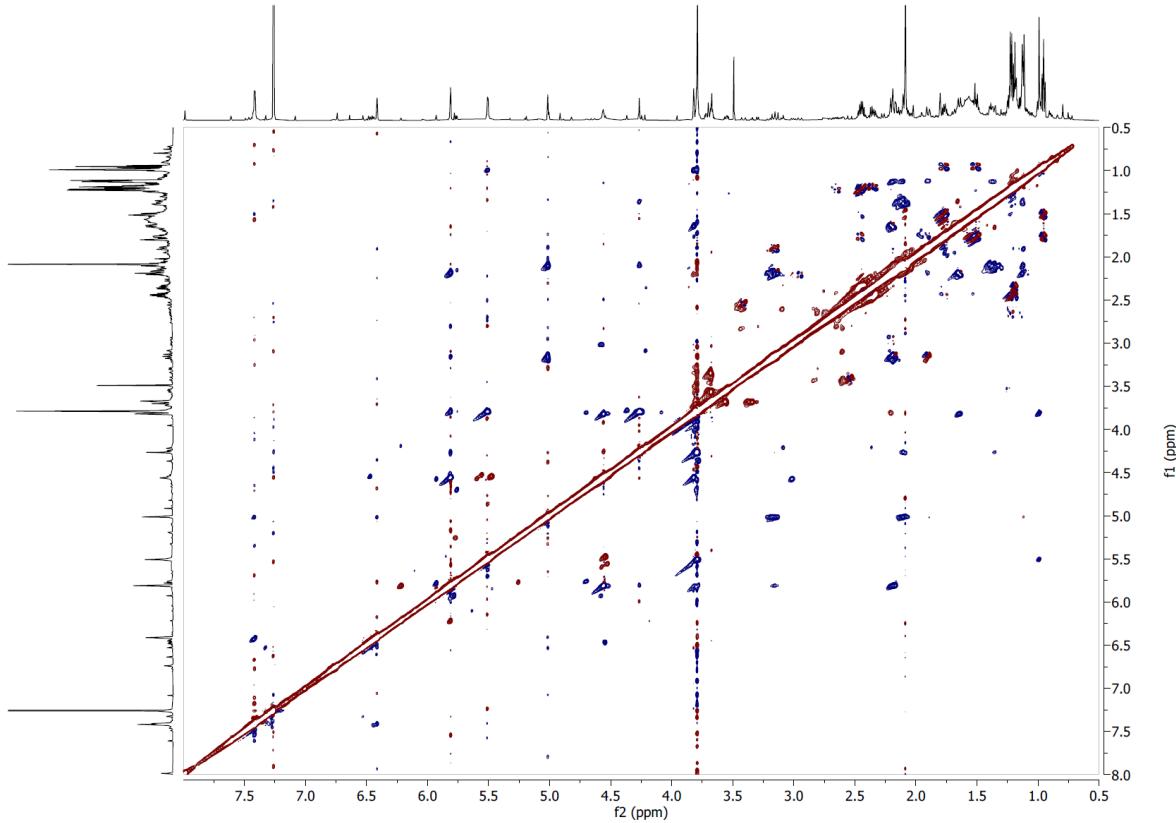
Supplementary Figure S4.2.87. ^{13}C -DEPTQ NMR spectrum of compound **15** in CDCl_3 at 151 MHz



Supplementary Figure S4.2.88. Edited HSQC NMR spectrum of compound **15** in CDCl_3

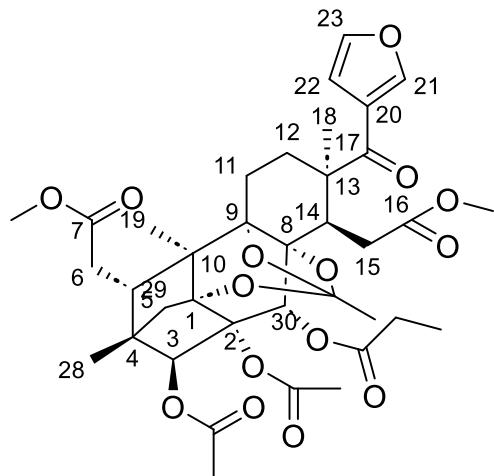


Supplementary Figure S4.2.89. HMBC NMR spectrum of compound **15** in CDCl_3



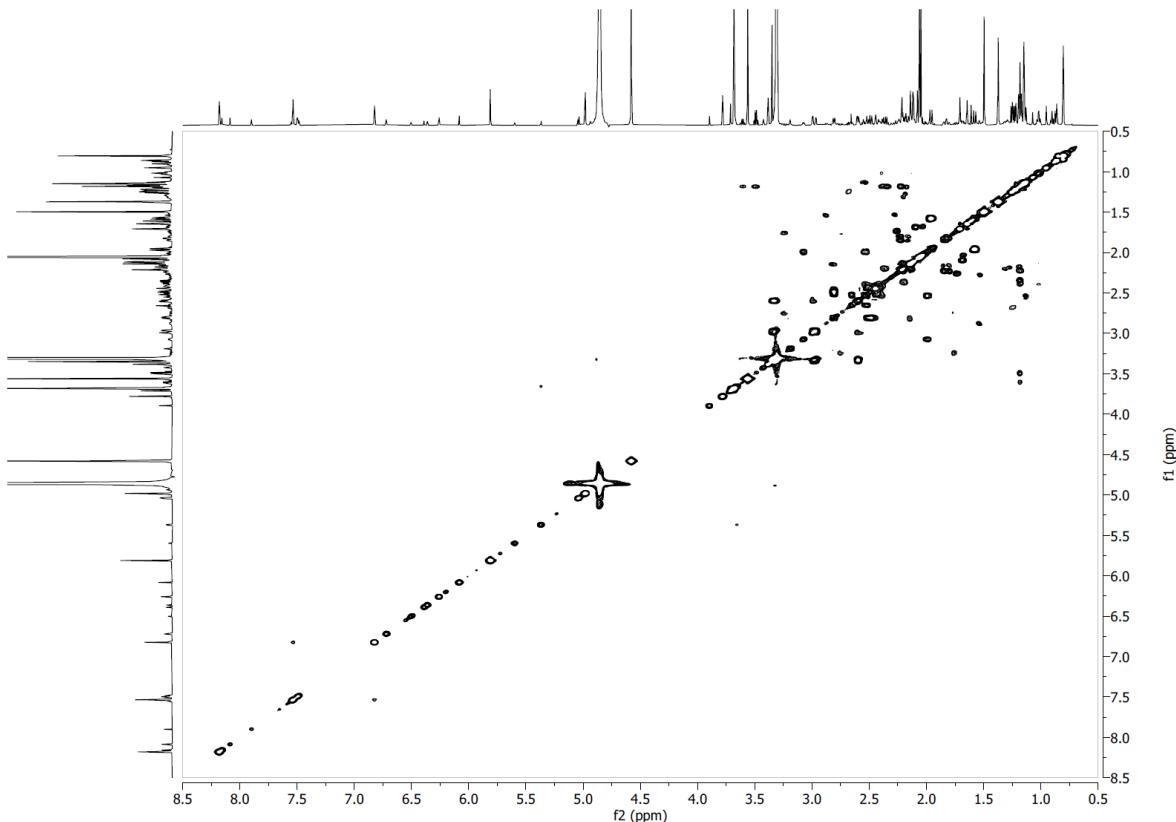
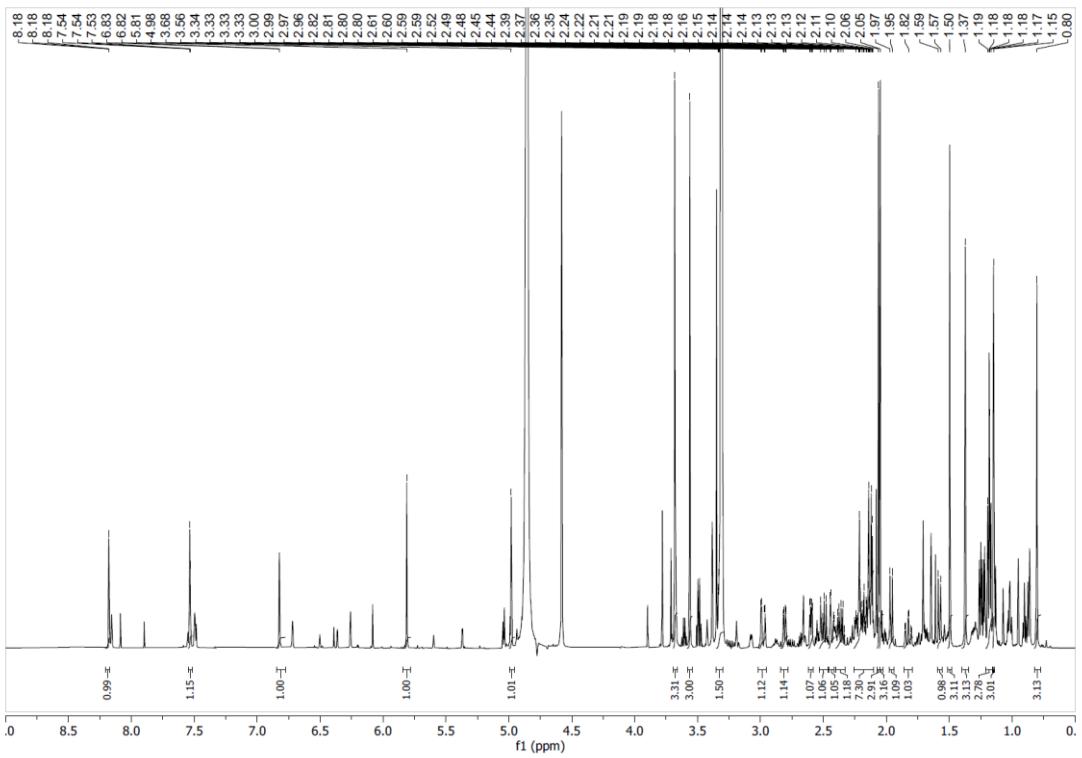
Supplementary Figure S4.2.90. ROESY NMR spectrum of compound **15** in CDCl_3

Compound 16. Amorphous white powder, HRESIMS m/z 687.2650 [M+H]⁺ (calculated for C₃₅H₄₃O₁₄Na, error 0.40 ppm), 685.2479 [M-H]⁻ (calculated for C₃₅H₄₁O₁₄, error -1.69 ppm); $[\alpha]_D^{20}$ -9 (c 0.0009 CHCl₃); UV (c 0.00 9, MeOH) λ_{max} 200, 226, 258 nm.

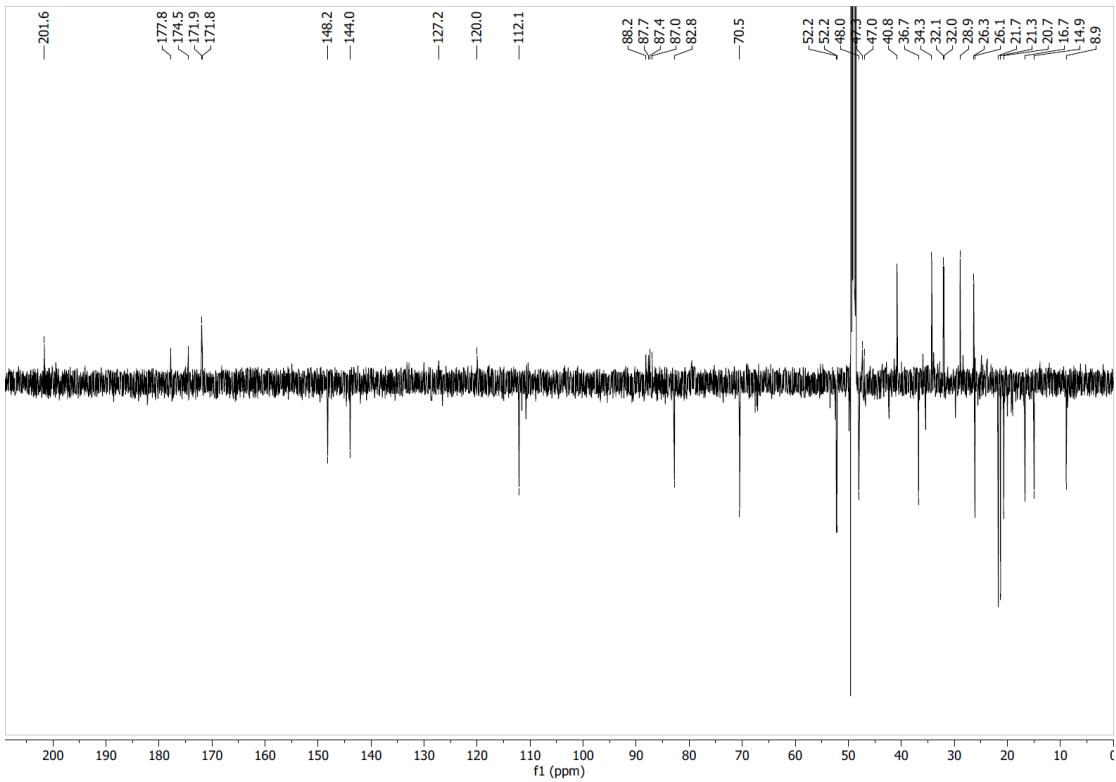


Chemical Formula: C₃₇H₄₆O₁₅
Exact Mass: 730.28

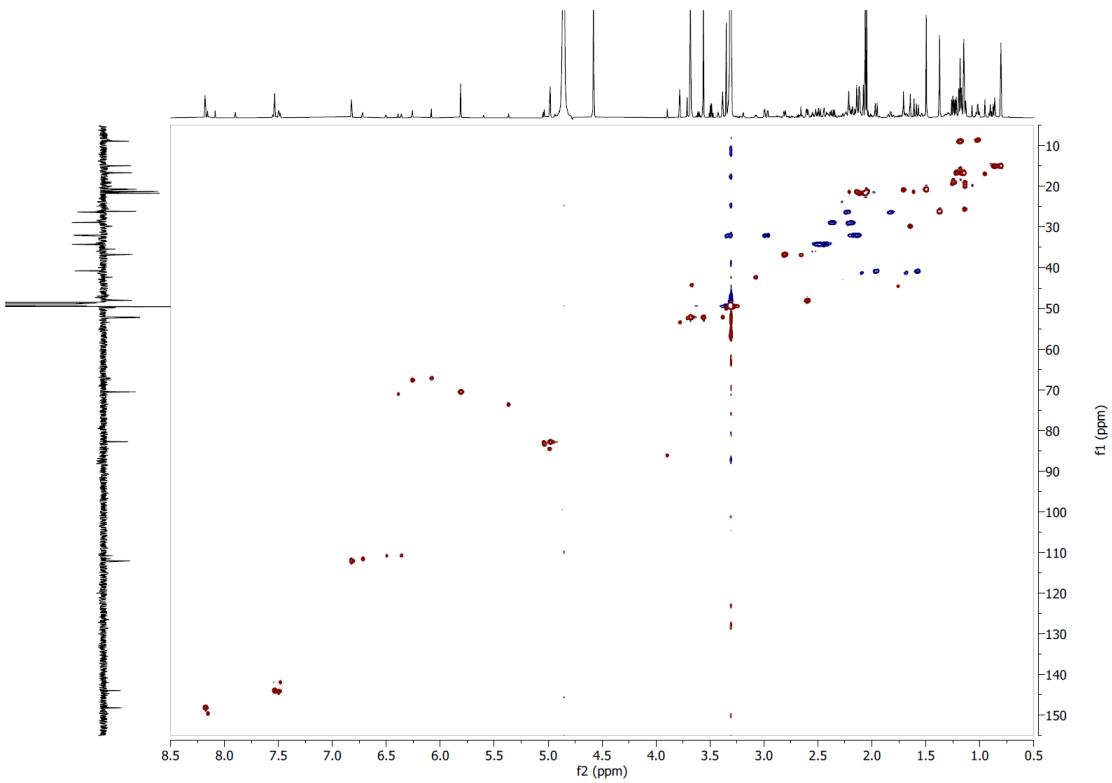
¹H NMR (CD₃OD, 600 MHz) δ 0.80 (3H, s, H₃-28), 1.15 (3H, s, H₃-19), 1.18 (3H, t, J = 7.7 Hz, H₃-30c), 1.37 (3H, s, H₃-18), 1.50 (3H, s, H₃-34), 1.58 (1H, d, J = 11.1 Hz, H-29''), 1.83 (1H, td, J = 14.5, 3.5 Hz, H-11 α), 1.96 (1H, d, J = 11.1 Hz, H-29'), 2.05 (3H, s, H₃-2b), 2.06 (3H, s, H₃-3b), 2.14 (1H, m, H-12''), 2.18 (1H, m, H-12'), 2.19 (1H, m, H-30b''), 2.24 (1H, m, H-11b), 2.37 (1H, m, H-30b'), 2.43 (1H, dd, J = 15.8, 2.6 Hz, H-6''), 2.50 (1H, dd, J = 15.8, 10.0 Hz, H-6'), 2.60 (1H, dd, J = 8.1, 3.3 Hz, H-14), 2.81 (1H, dd, J = 10.0, 2.6 Hz, H-5), 2.98 (1H, dd, J = 17.3, 3.3 Hz, H-15''), 3.32 (1H, dd, J = 17.3, 3.3 Hz, H-15'), 3.56 (3H, s, OCH₃), 3.68 (3H, s, 16-OCH₃), 4.98 (1H, s, H-3), 5.81 (1H, s, H-30), 6.82 (1H, d, J = 1.7 Hz, H-22), 7.54 (1H, t, J = 1.7 Hz, H-23), 8.18 (1H, t, J = 1.7 Hz, H-21); ¹³C NMR (CD₃OD, 151 MHz) δ 8.9 (CH₃-30c), 14.9 (CH₃-28), 16.7 (CH₃-19), 20.7 (CH₃-34), 21.3 (CH₃-2b), 21.7 (CH₃-3b), 26.1 (CH₃-18), 26.3 (CH₂-11), 28.9 (CH₂-30b), 32.0 (CH₂-12), 32.1 (CH₂-15), 34.3 (CH₂-6), 36.7 (CH-5), 40.8 (CH₂-29), 47.0 (C-10), 47.3 (C-4), 48.0 (CH-14), 49.0 (C-13), 52.2 (16-OCH₃), 52.2 (OCH₃), 70.5 (CH-30), 82.8 (CH-3), 87.0 (C-1), 87.4 (C-8), 87.7 (C-2), 88.2 (C-9), 112.1 (CH-22), 120.0 (C-33), 127.2 (C-20), 144.0 (CH-23), 148.2 (CH-21), 171.8 (C-30a), 171.9 (C-2a, C-3a), 174.5 (C-7), 177.8 (C-16), 201.6 (C-17).
Supplementary Figures S4.2.91-S4.2.96.



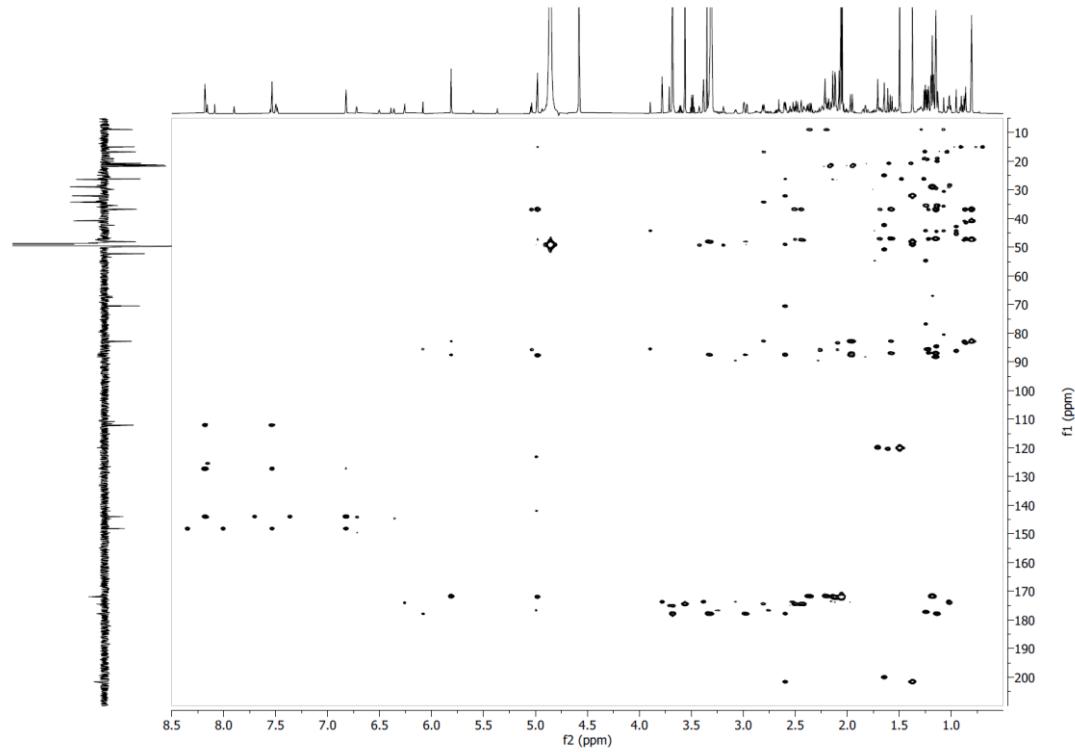
Supplementary Figure S4.2.92. COSY NMR spectrum of compound 16 in CD_3OD



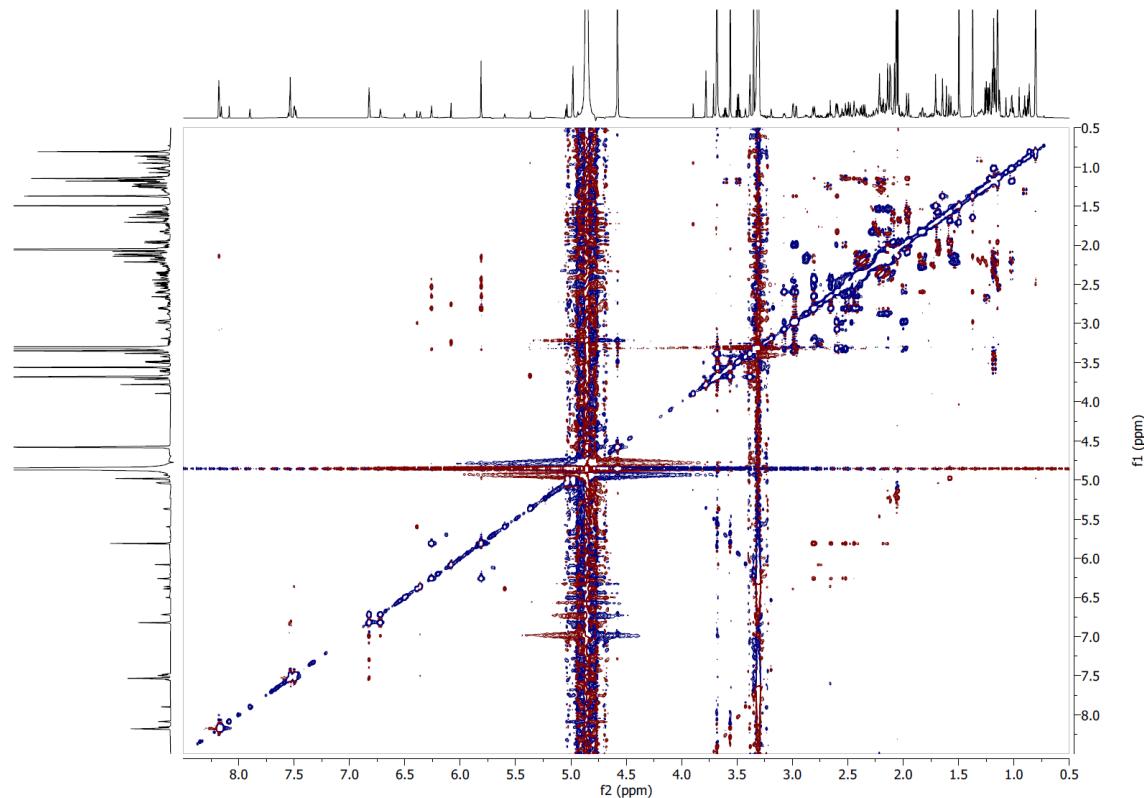
Supplementary Figure S4.2.93. ^{13}C -DEPTQ NMR spectrum of compound **16** in CD_3OD at 151 MHz



Supplementary Figure S4.2.94. Edited HSQC NMR spectrum of compound **16** in CD_3OD

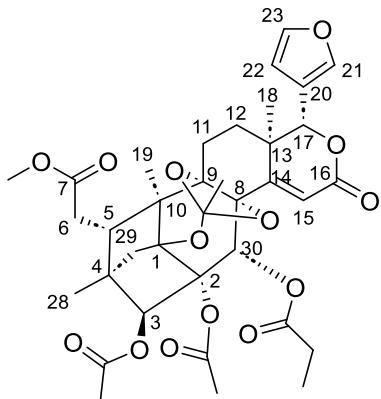


Supplementary Figure S4.2.95. HMBC NMR spectrum of compound **16** in CD_3OD



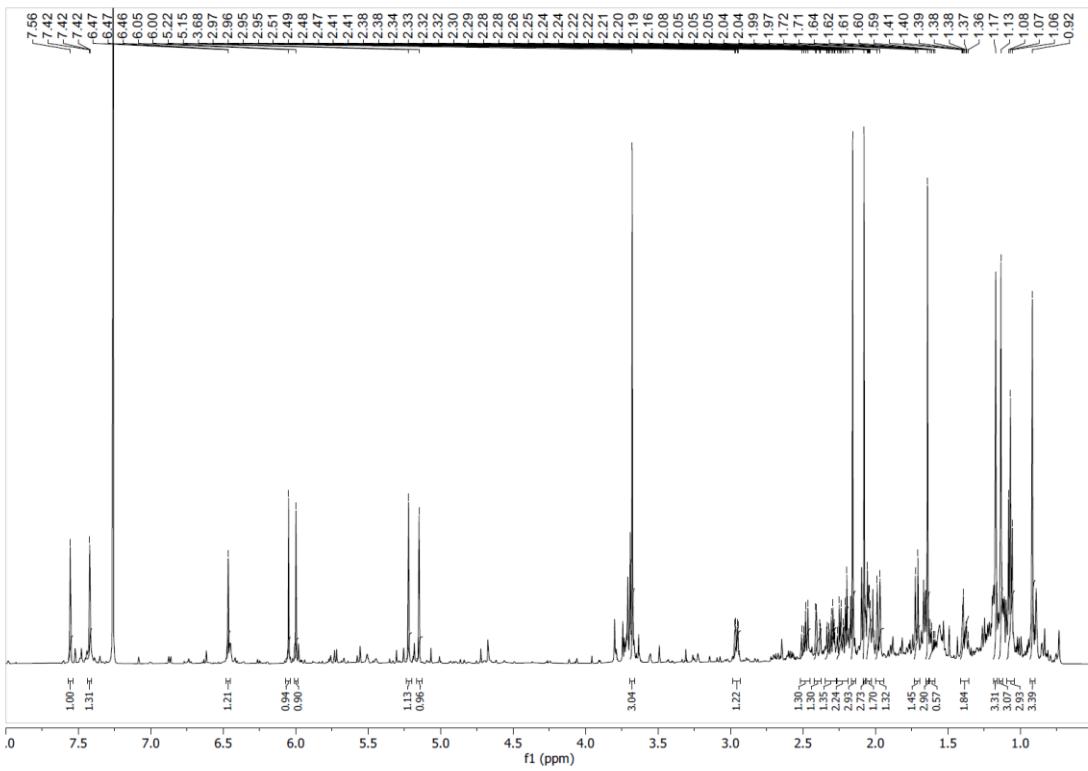
Supplementary Figure S4.2.96. ROESY NMR spectrum of compound **16** in CD_3OD

Compound 17. Amorphous white powder, HRESIMS m/z 699.2648 [M+H]⁺ (calculated for C₃₆H₄₃O₁₄, error 0.22 ppm); $[\alpha]_D^{20} -4$ (c 0.003 CHCl₃); UV (c 0.003, MeOH) λ_{max} 200 239 nm.

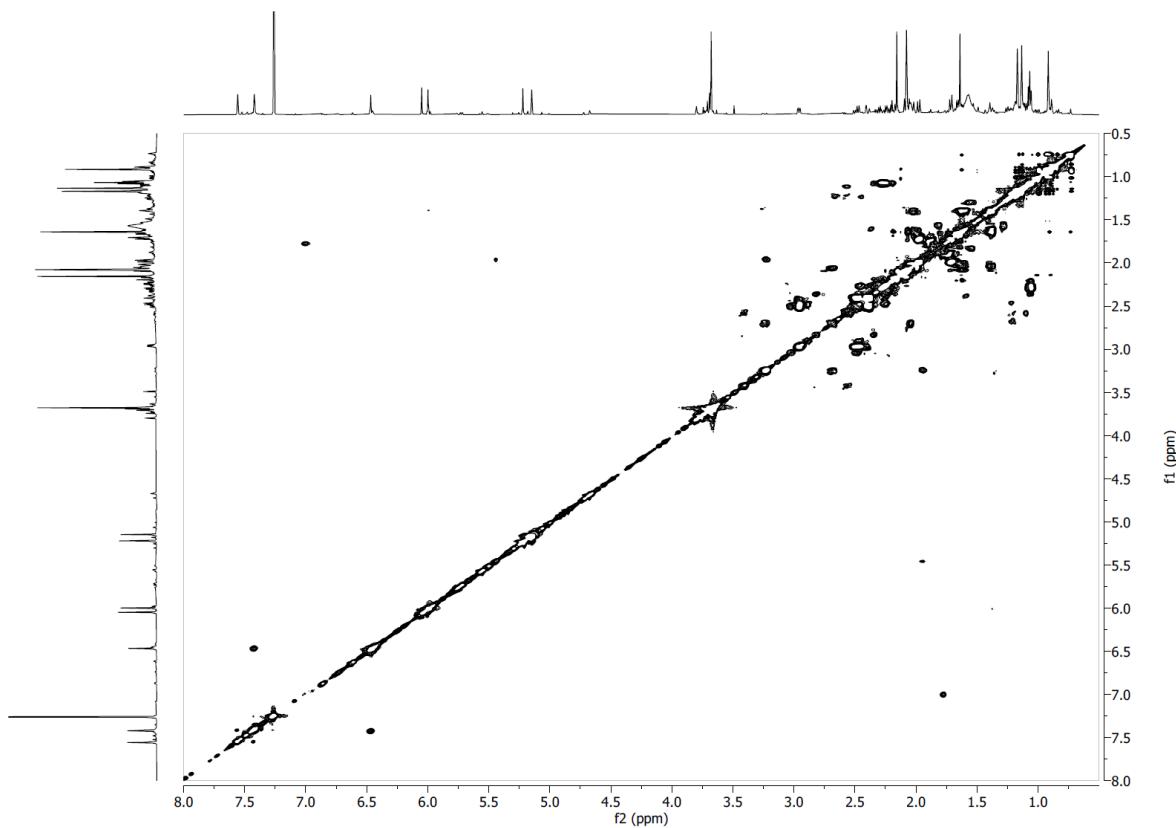


Chemical Formula: C₃₆H₄₂O₁₄
Exact Mass: 698.26

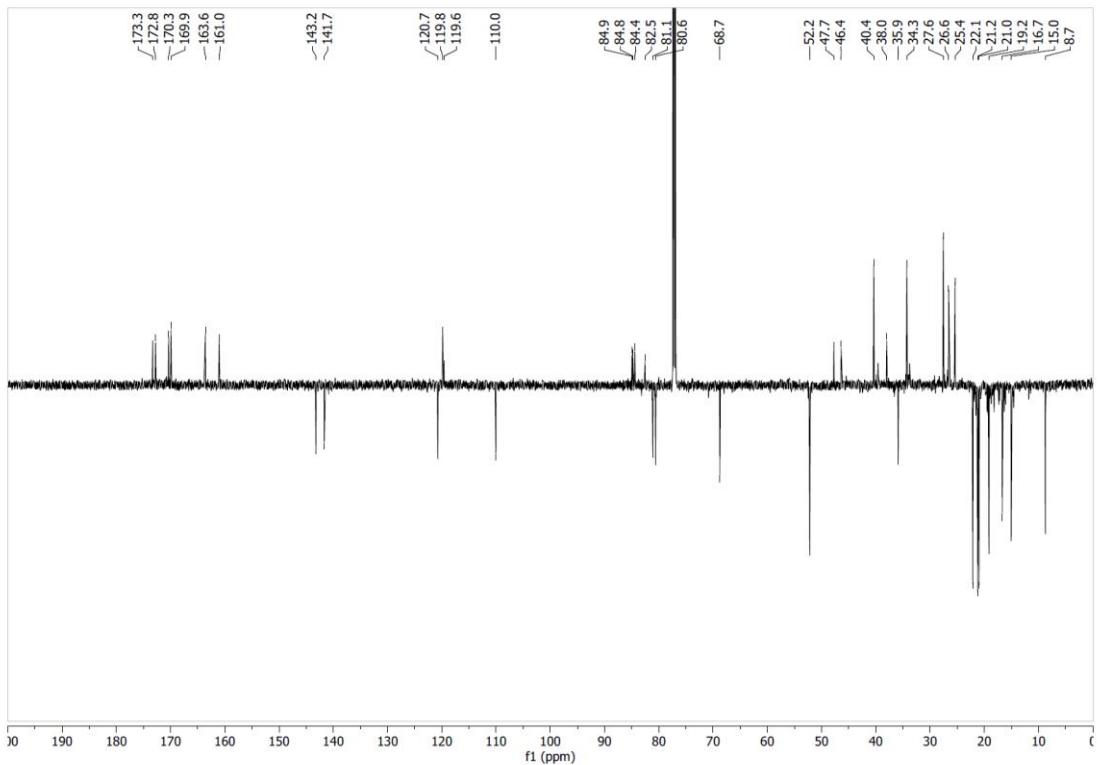
¹H NMR (CDCl₃, 600 MHz) δ 0.92 (3H, s, H₃-28), 1.07 (3H, t, J = 7.5 Hz, H₃-30c), 1.13 (3H, s, H₃-18), 1.17 (3H, s, H₃-19), 1.38 (1H, m, H-12''), 1.61 (1H, m, H-12'), 1.64 (3H, s, H₃-34), 1.71 (1H, d, J = 11.1 Hz, H-29''), 1.98 (1H, d, J = 11.1 Hz, H-29'), 2.05 (2H, m, H₂-11), 2.08 (3H, s, H₃-3b), 2.16 (3H, s, H₃-2b), 2.27 (1H, m, H-30b''), 2.30 (1H, m, H-30b'), 2.39 (1H, dd, J = 17.0, 2.8 Hz, H-6''), 2.49 (1H, dd, J = 17.0, 9.9 Hz, H-6'), 2.96 (1H, dd, J = 9.9, 2.8 Hz, H-5), 3.68 (3H, s, OCH₃), 5.15 (1H, s, H-17), 5.22 (1H, m, H-3), 6.00 (1H, s, H-30), 6.05 (1H, s, H-15), 6.47 (1H, d, J = 1.7 Hz, H-22), 7.42 (1H, d, J = 1.7 Hz, H-23), 7.56 (1H, s, H-21); ¹³C NMR (CDCl₃, 151 MHz) δ 8.7 (CH₃-30c), 15.0 (CH₃-28), 16.7 (CH₃-19), 19.2 (CH₃-18), 21.0 (CH₃-3b), 21.2 (CH₃-34), 22.1 (CH₃-2b), 25.4 (CH₂-11), 26.6 (CH₂-12), 27.6 (CH₂-30b), 34.3 (CH₂-6), 35.9 (CH-5), 38.0 (C-13), 40.4 (CH₂-29), 46.4 (C-4), 47.7 (C-10), 52.2 (OCH₃), 68.7 (CH-30), 80.6 (CH-17), 81.1 (CH-3), 82.5 (C-8), 84.4 (C-9), 84.8 (C-1), 84.9 (C-2), 110.0 (CH-22), 119.6 (C-33), 119.8 (C-20), 120.7 (CH-15), 141.7 (CH-21), 143.2 (CH-23), 161.0 (C-14), 163.6 (C-16), 169.9 (C-3a), 170.3 (C-2a), 172.8 (C-7), 173.3 (C-30a). Supplementary Figures S4.2.97-S4.2.102.



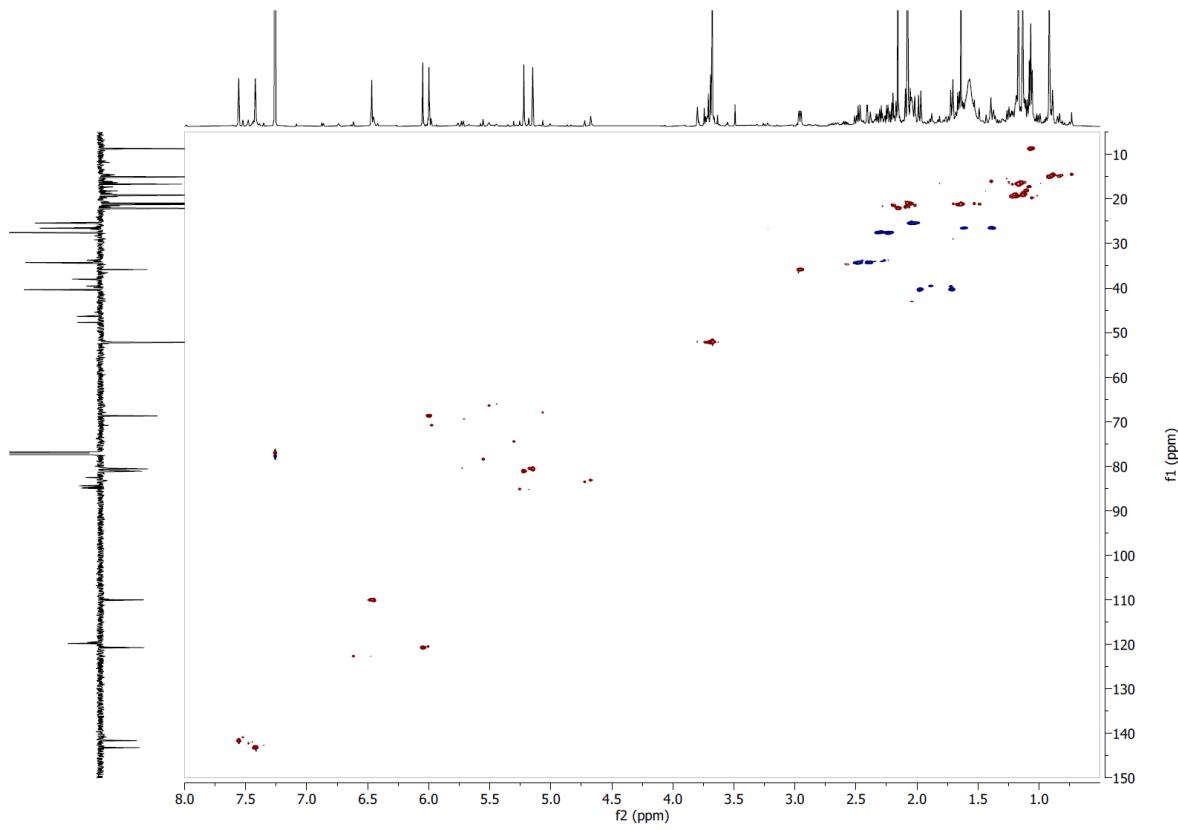
Supplementary Figure S4.2.97. ^1H NMR spectrum of compound **17** in CDCl_3 at 600 MHz



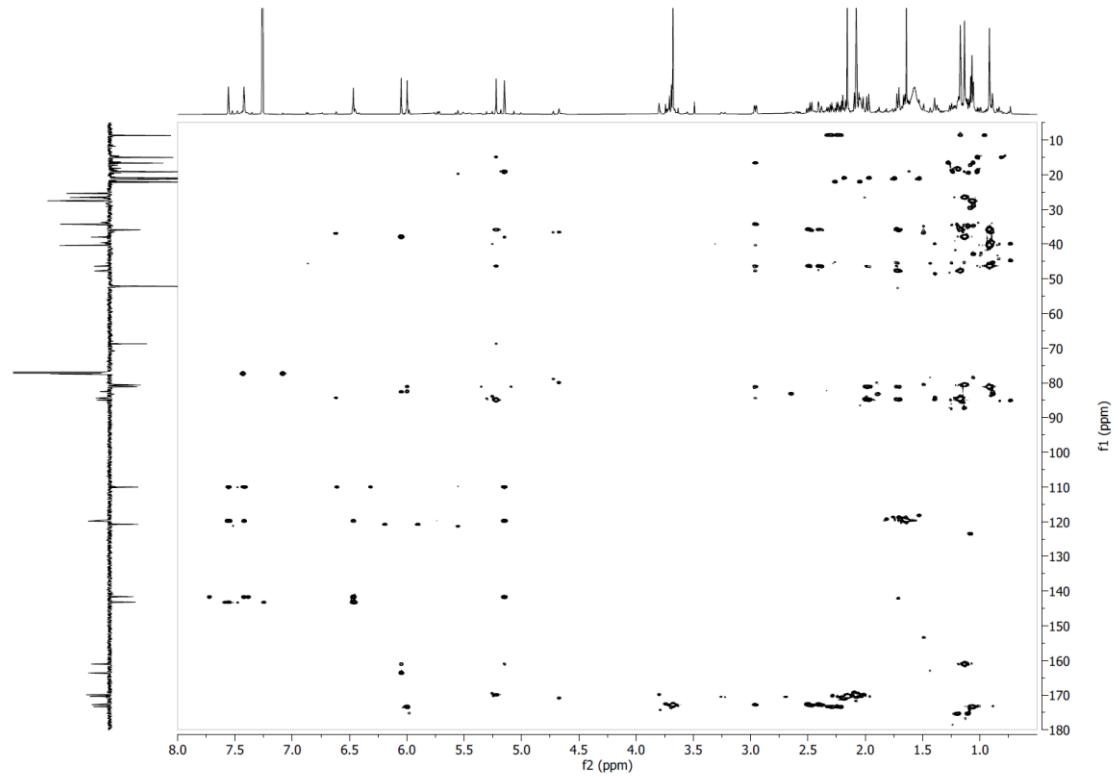
Supplementary Figure S4.2.98. COSY NMR spectrum of compound **17** in CDCl_3



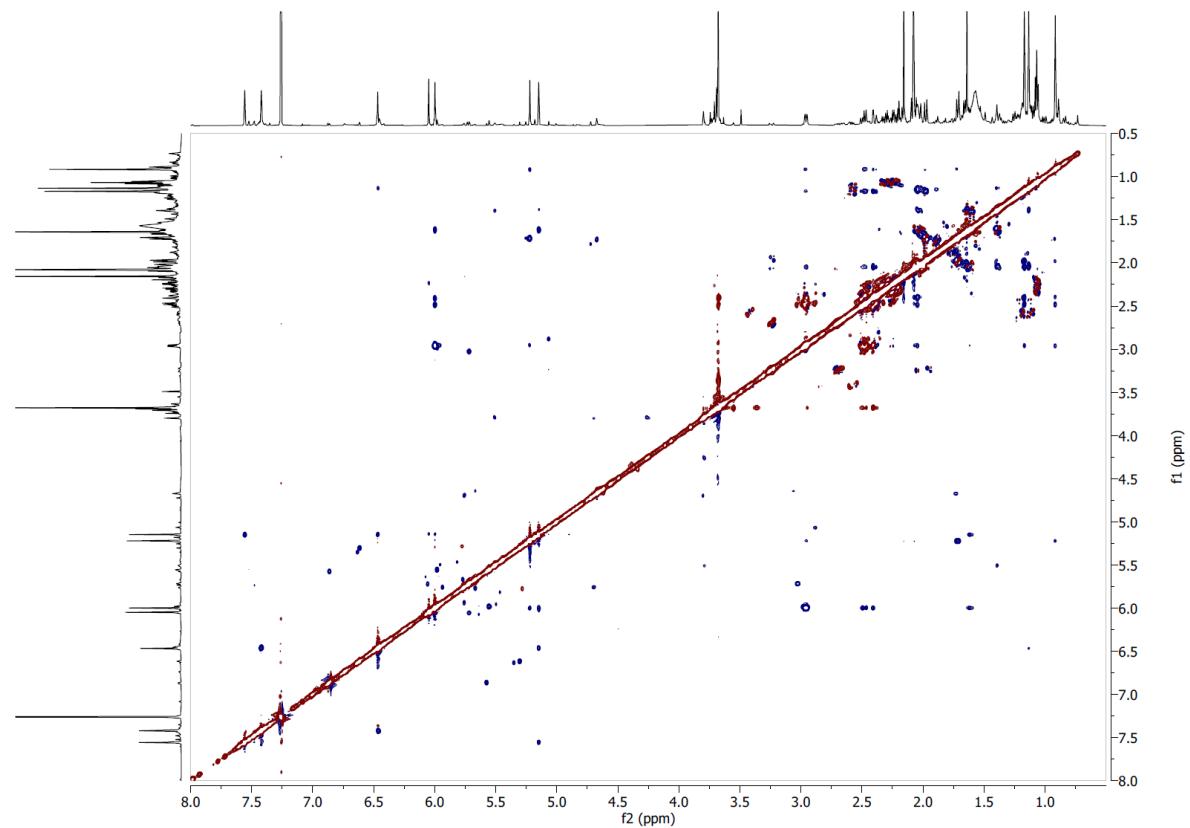
Supplementary Figure S4.2.99. ^{13}C -DEPTQ NMR spectrum of compound **17** in CDCl_3 at 151 MHz



Supplementary Figure S4.2.100. Edited HSQC NMR spectrum of compound **17** in CDCl_3

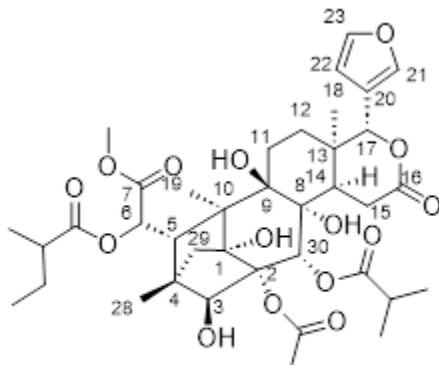


Supplementary Figure S4.2.101. HMBC NMR spectrum of compound **17** in CDCl_3



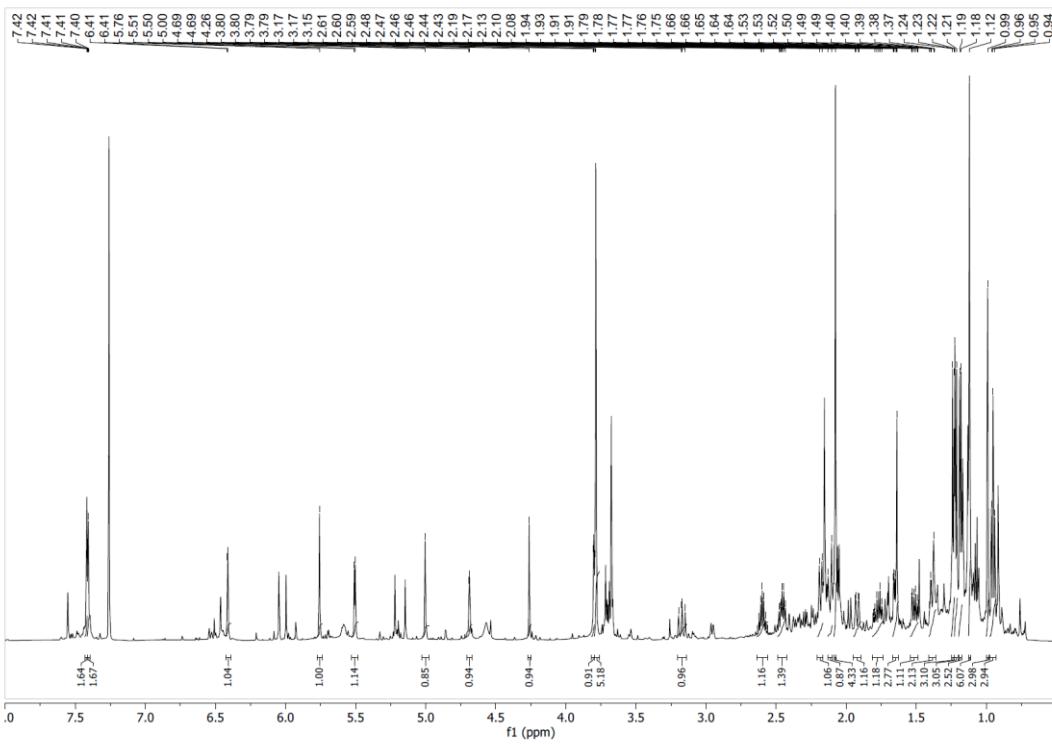
Supplementary Figure S4.2.102. ROESY NMR spectrum of compound **17** in CDCl_3

Compound 18. Amorphous white powder, HRESIMS m/z 771.3188 [M+Na]⁺ (calculated for C₃₈H₅₂O₁₅Na, error -1.31 ppm), 747.3263 [M-H]⁻ (calculated for C₃₈H₅₁O₁₅, error 0.51 ppm); $[\alpha]_D^{20}$ -2.5 (c 0.007 CHCl₃); UV (c 0.007, MeOH) λ_{max} 200, 241 nm.

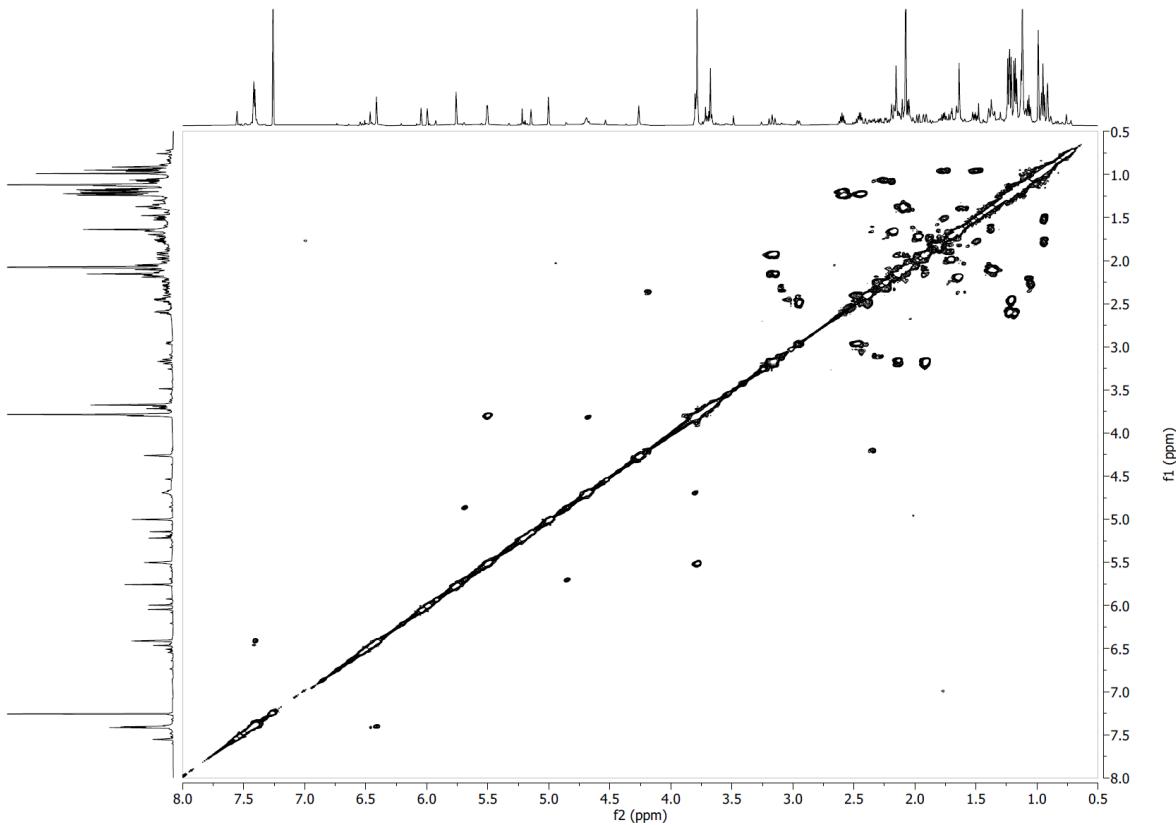


Chemical Formula: C₃₈H₅₂O₁₅
Exact Mass: 748.33

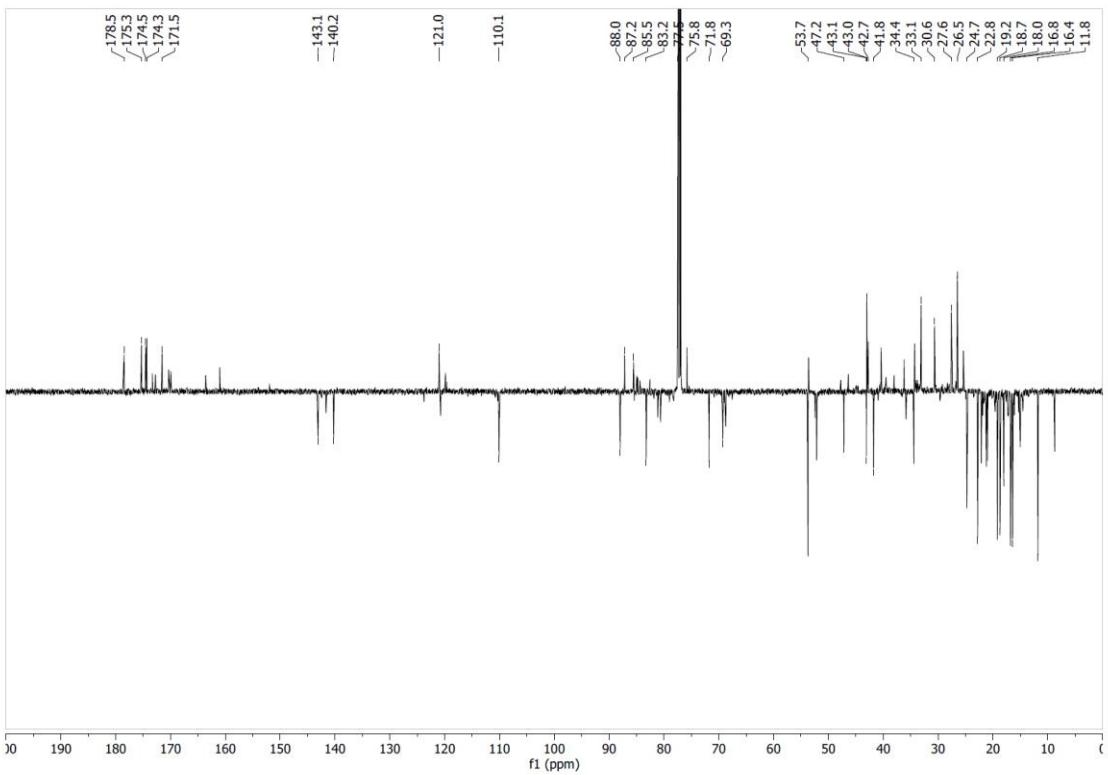
¹H NMR (CDCl₃, 600 MHz) δ 0.95 (3H, t, J = 7.4 Hz, H₃-6d), 0.99 (3H, s, H₃-28), 1.12 (6H, s, H₃-18, H₃-19), 1.18 (3H, d, J = 7.1 Hz, H₃-30d), 1.22 (3H, d, J = 7.1 Hz, H₃-6e), 1.24 (3H, d, J = 7.1 Hz, H₃-30c), 1.36 (1H, m, H-11a), 1.39 (1H, m, H-12a), 1.51 (1H, m, H-6c^{''}), 1.65 (1H, d, J = 11.0 Hz, H-29^{''}), 1.77 (1H, m, H-6c[']), 1.92 (1H, dd, J = 13.4, 3.2 Hz, H-14), 2.08 (3H, s, H₃-2b), 2.11 (1H, m, H-11b, H-12b), 2.14 (1H, m, H-15a), 2.18 (1H, d, J = 11.0 Hz, H-29[']), 2.46 (1H, m, H-6b), 2.60 (1H, hept, J = 7.1 Hz, H-30b), 3.17 (1H, dd, J = 15.6, 13.4 Hz, H-15 β), 3.79 (3H, s, OCH₃), 3.79 (1H, overlapped, H-5), 3.80 (1H, d, J = 2.3 Hz, H-3), 4.26 (1H, s, OH-9), 4.69 (1H, d, J = 2.3 Hz, OH-3), 5.00 (1H, s, H-17), 5.51 (1H, d, J = 4.1 Hz, H-6), 5.76 (1H, s, H-30), 6.41 (1H, d, J = 1.7 Hz, H-22), 7.41 (1H, t, J = 1.7 Hz, H-23), 7.42 (1H, d, J = 1.7 Hz, H-21); ¹³C NMR (CDCl₃, 151 MHz) δ 11.8 (CH₃-6d), 16.4 (CH₃-28), 16.8 (CH₃-6e), 18.0 (CH₃-19), 18.7 (CH₃-30d), 19.2 (CH₃-30c), 22.8 (CH₃-2b), 24.7 (CH₃-18), 26.5 (CH₂-6c), 27.6 (CH₂-11), 30.6 (CH₂-12), 33.1 (CH₂-15), 34.4 (CH-30b), 41.8 (CH-6b), 42.7 (C-4), 43.0 (CH₂-29), 43.1 (CH-5), 47.2 (CH-14), 53.7 (OCH₃), 69.3 (CH-30), 71.8 (CH-6), 75.8 (C-9), 77.5 (C-8), 83.2 (CH-17), 85.5 (C-2), 87.2 (C-1), 88.0 (CH-3), 110.1 (CH-22), 121.0 (C-20), 140.2 (CH-21), 143.1 (C-H23), 171.5 (C-2a), 174.3 (C-7), 174.5 (C-16), 175.3 (C-6a), 178.5 (C-30a). Supplementary Figures S4.2.103-S4.2.108.



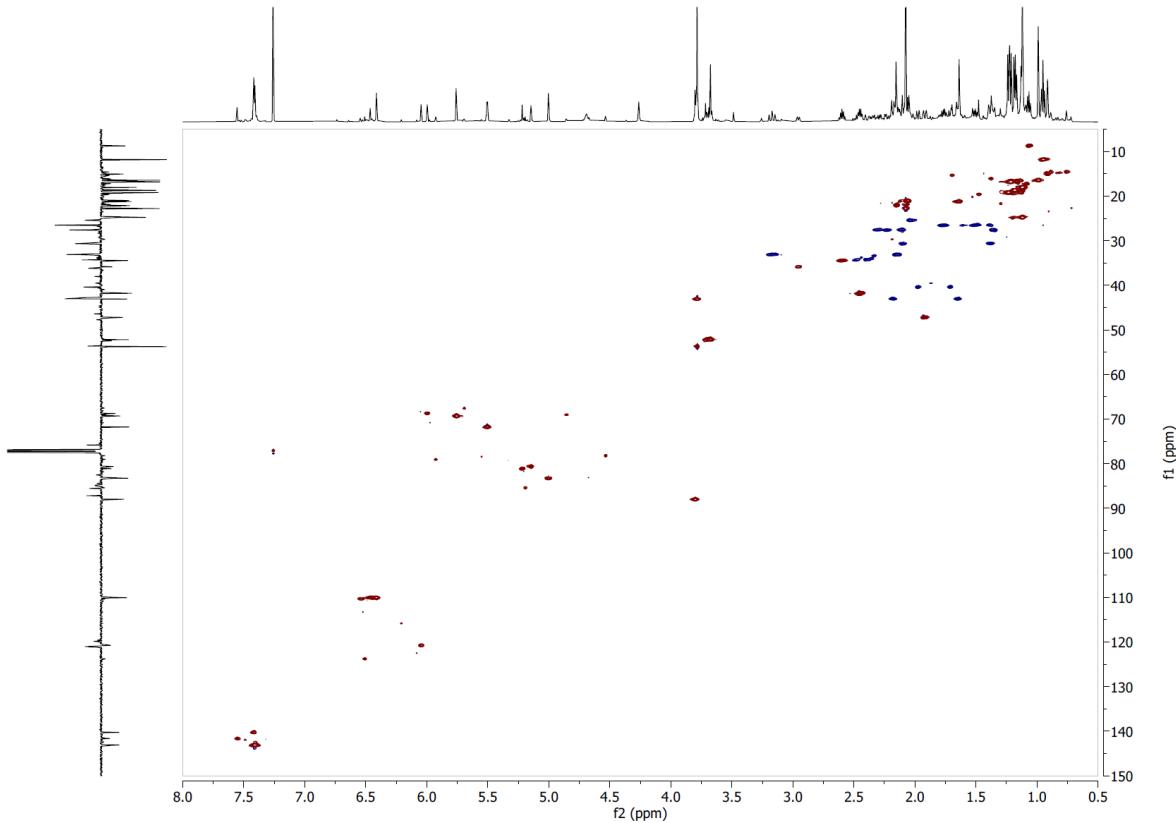
Supplementary Figure S4.2.103. ^1H NMR spectrum of compound **18** in CDCl_3 at 600 MHz



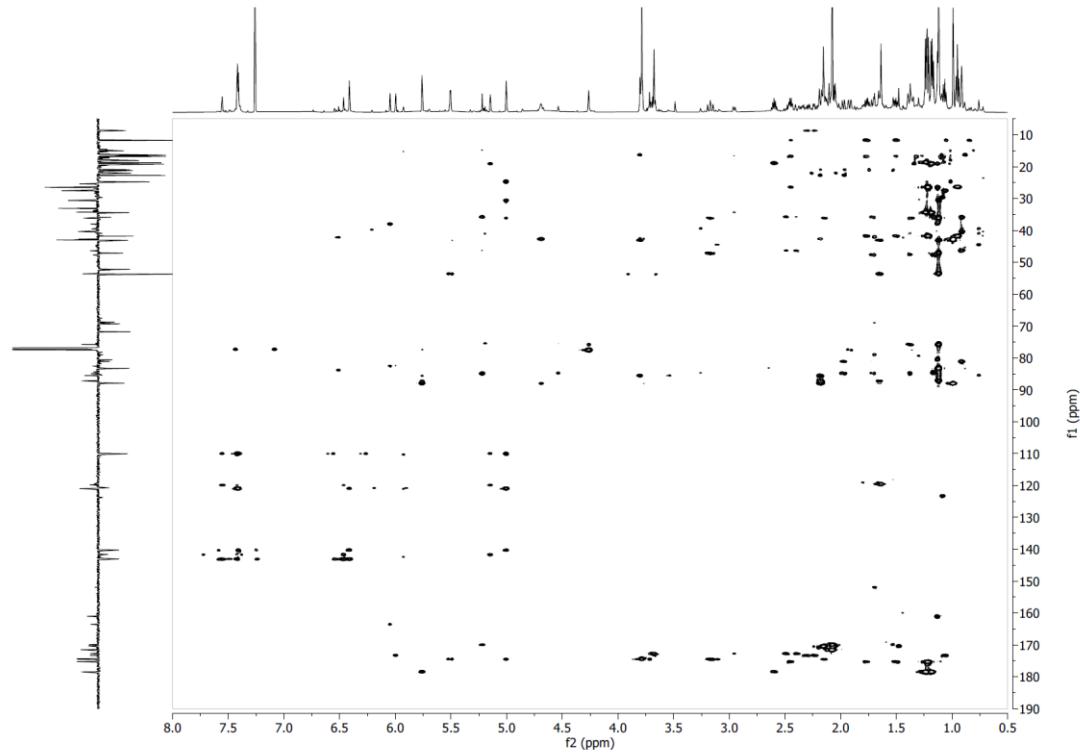
Supplementary Figure S4.2.104. COSY NMR spectrum of compound **18** in CDCl_3



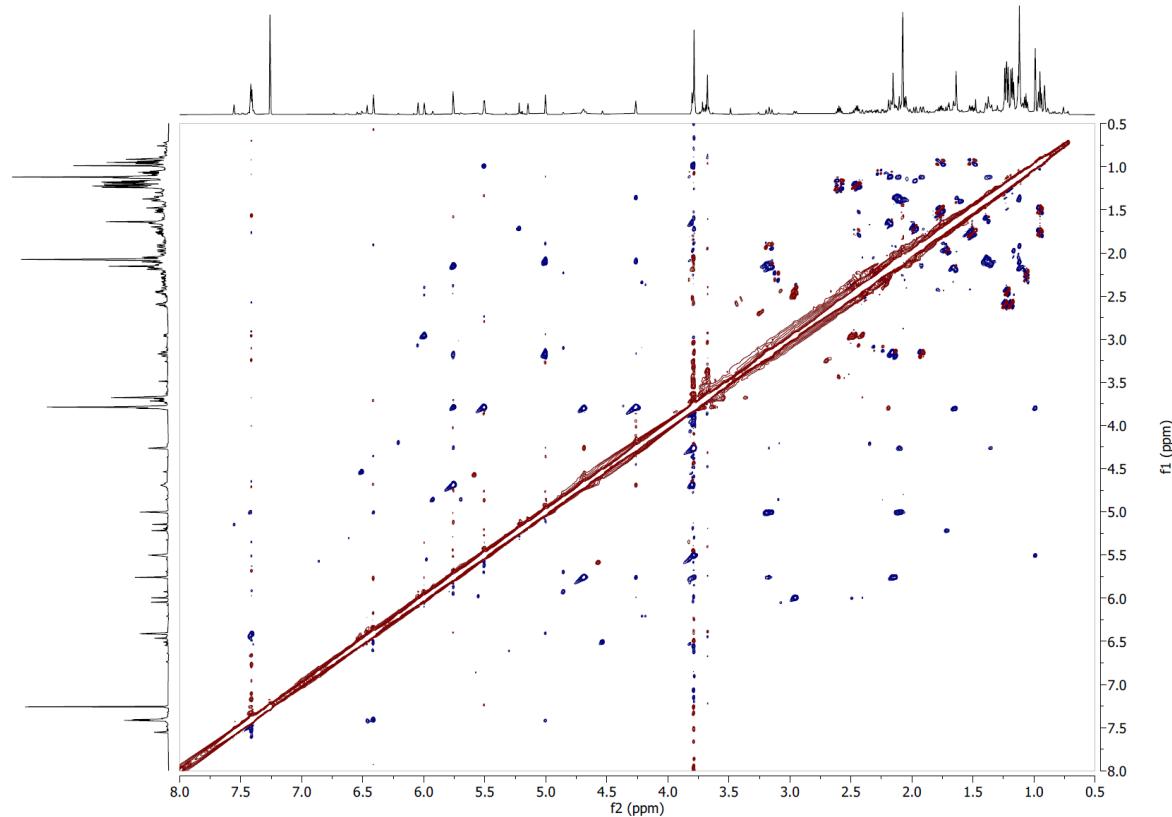
Supplementary Figure S4.2.105. ^{13}C -DEPTQ NMR spectrum of compound **18** in CDCl_3 at 151 MHz



Supplementary Figure S4.2.106. Edited HSQC NMR spectrum of compound **18** in CDCl_3

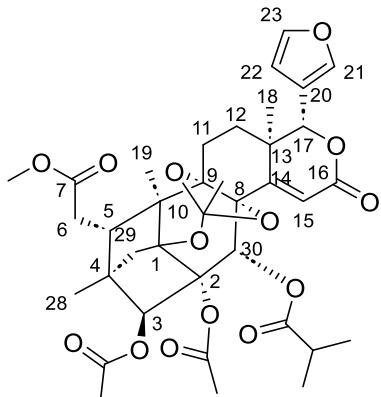


Supplementary Figure S4.2.107. HMBC NMR spectrum of compound **18** in CDCl_3



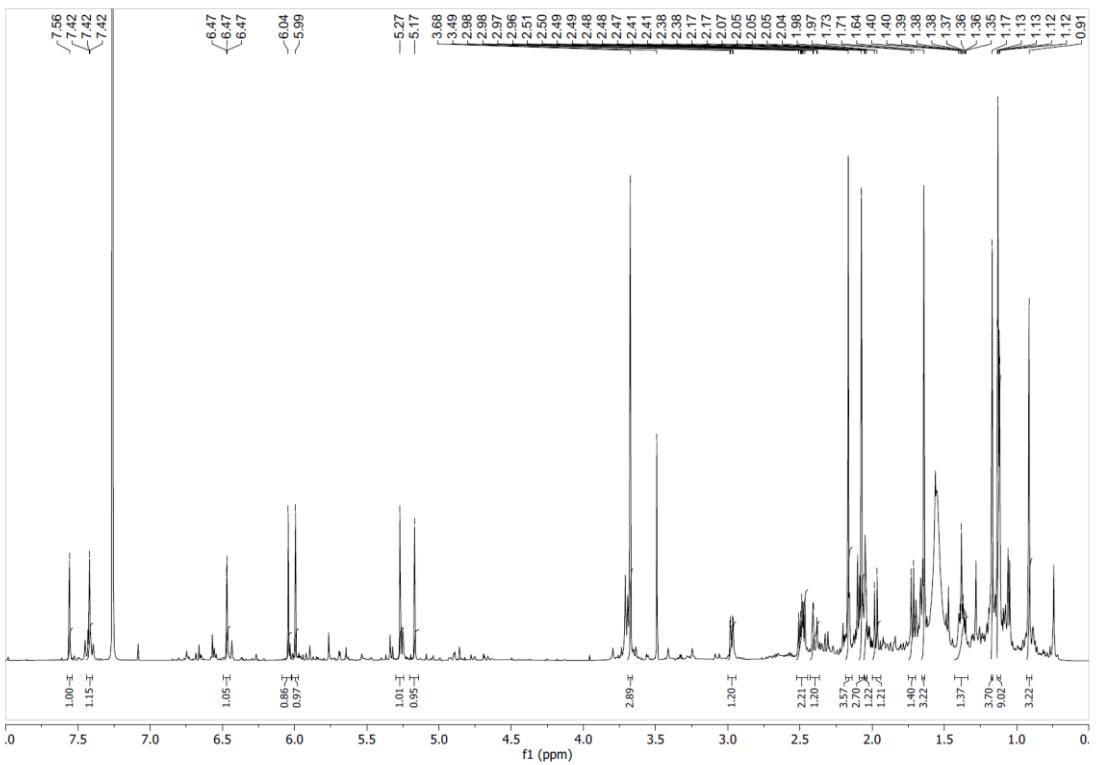
Supplementary Figure S4.2.108. ROESY NMR spectrum of compound **18** in CDCl_3

Compound 19. Amorphous white powder, HRESIMS m/z 713.2805 [M+H]⁺ (calculated for C₃₇H₄₅O₁₄, error 0.19 ppm); $[\alpha]_D^{20}$ 2 (c 0.001 CHCl₃); UV (c 0.001, MeOH) λ_{max} 200, 240 nm.

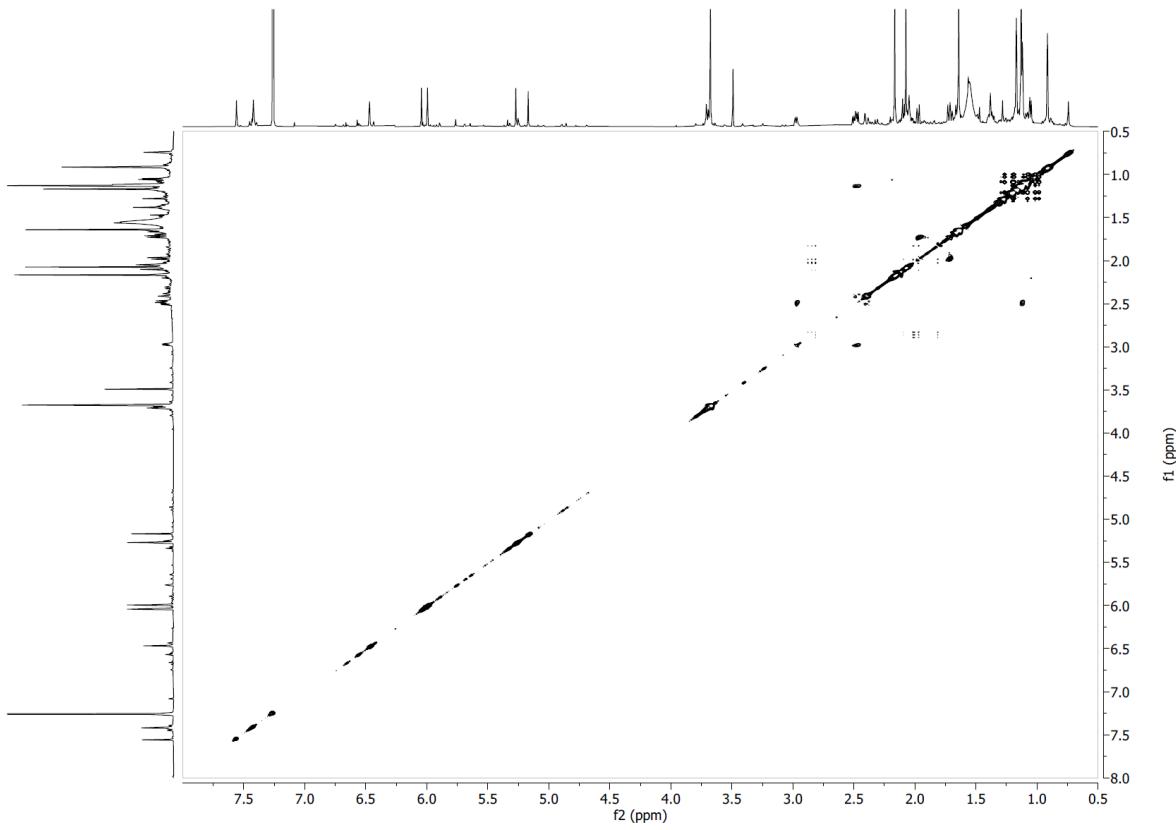


Chemical Formula: C₃₇H₄₄O₁₄
Exact Mass: 712.27

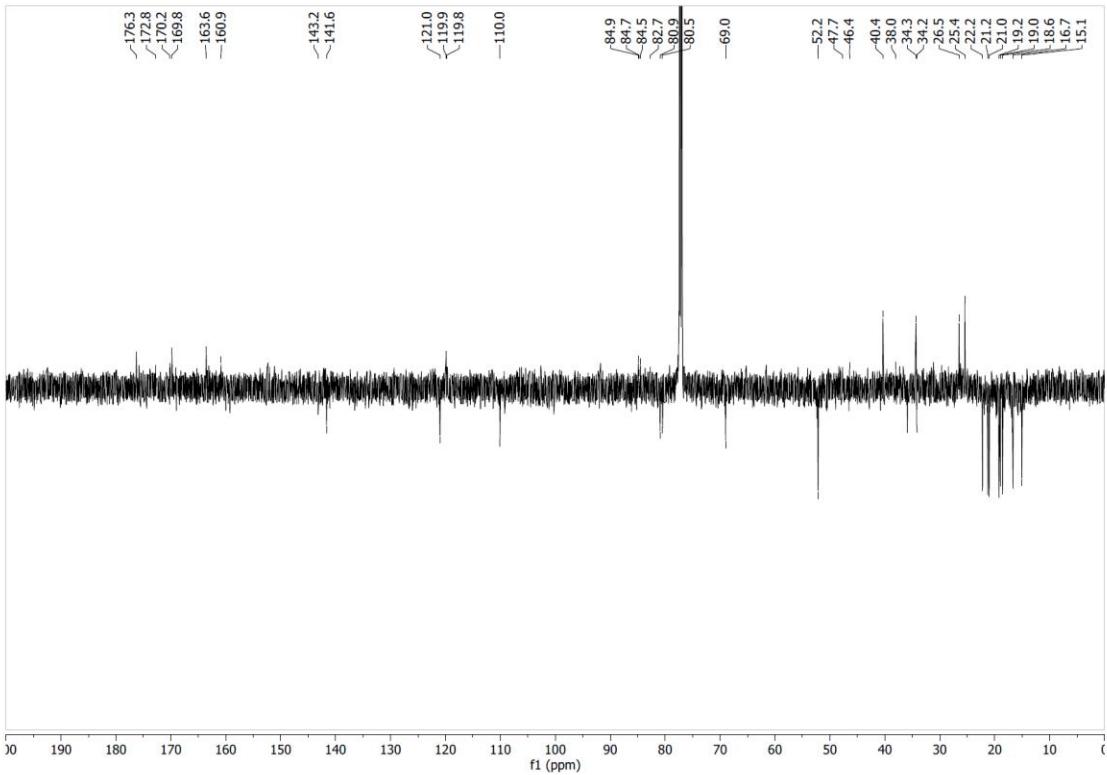
¹H NMR (CDCl₃, 600 MHz) δ 0.91 (3H, s, H₃-28), 1.13 (9H, m, H₃-18, H₃-30c, H₃-30d), 1.17 (3H, s, H₃-19), 1.38 (1H, m, H-12''), 1.64 (1H, overlapped, H-12'), 1.64 (3H, s, H₃-34), 1.72 (1H, d, J = 11.0 Hz, H-29''), 1.97 (1H, d, J = 11.0 Hz, H-29'), 2.05 (2H, m, H₂-11), 2.07 (3H, s, V3b), 2.17 (3H, s, H₃-2b), 2.40 (1H, dd, J = 17.0, 2.8 Hz, H-6''), 2.49 (2H, m, H-6', H-30b), 2.97 (1H, dd, J = 9.9, 2.8 Hz, H-5), 3.68 (3H, s, OCH₃), 5.17 (1H, s, H-17), 5.27 (1H, s, H-3), 5.99 (1H, s, H-30), 6.04 (1H, s, H-15), 6.47 (1H, d, J = 1.7 Hz, H-22), 7.42 (1H, d, J = 1.7 Hz, H-23), 7.56 (1H, s, H-21); ¹³C NMR (CDCl₃, 151 MHz) δ 15.1 (CH₃-28), 16.7 (CH₃-19), 18.6 (CH₃-30d), 19.0 (CH₃-30c), 19.2 (CH₃-18), 21.0 (CH₃-3b), 21.2 (CH₃-34), 22.2 (CH₃-2b), 25.4 (CH₂-11), 26.5 (CH₂-12), 34.2 (CH-30b), 34.3 (CH₂-6), 38.0 (C-13), 40.4 (CH₂-29), 46.4 (C-4), 47.7 (C-10), 52.2 (OCH₃), 69.0 (CH-30), 80.5 (CH-17), 80.9 (CH-3), 82.7 (C-8), 84.5 (C-9), 84.7 (C-1), 84.9 (C-2), 110.0 (CH-22), 119.8 (C-33), 119.9 (C-20), 121.0 (CH-15), 141.6 (CH-21), 143.2 (CH-23), 160.9 (C-14), 163.6 (C-16), 169.8 (C-3a), 170.2, 172.8 (C-7), 176.3 (30a). **Supplementary Figures S4.2.109–S4.2.114.**



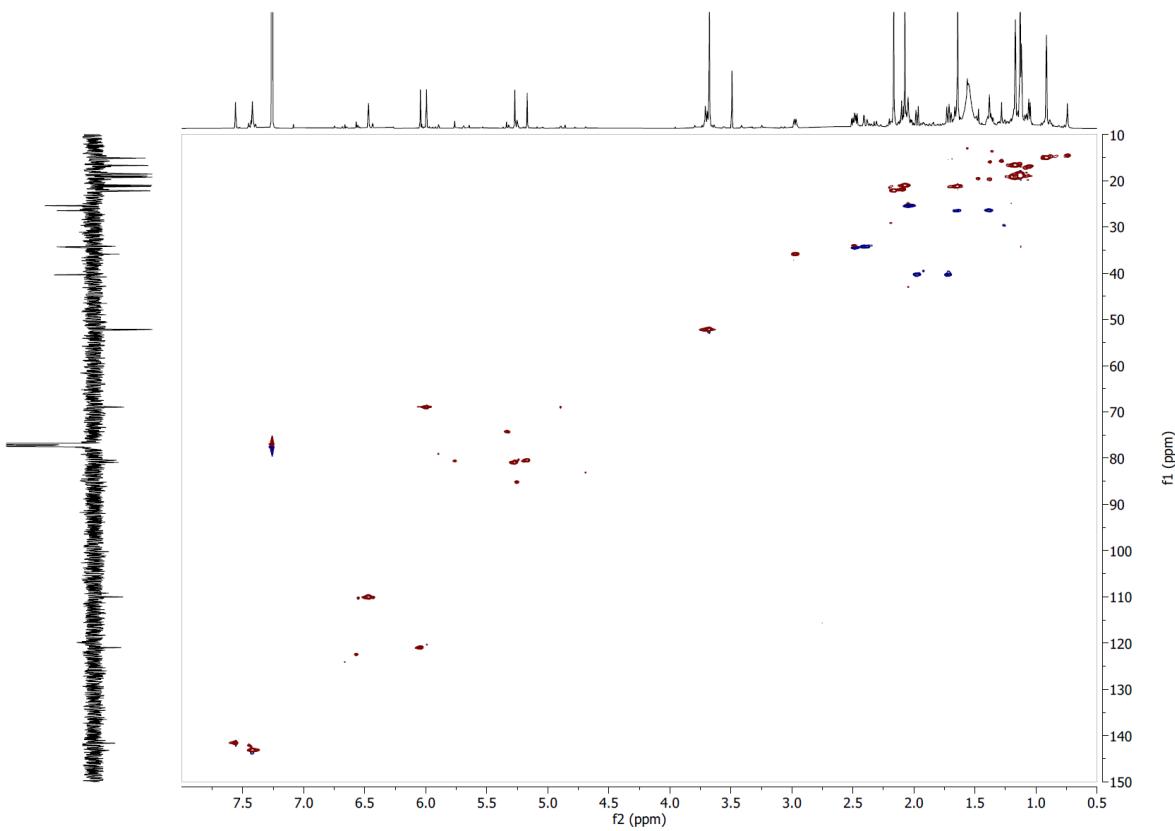
Supplementary Figure S4.2.109. ^1H NMR spectrum of compound **19** in CDCl_3 at 600 MHz



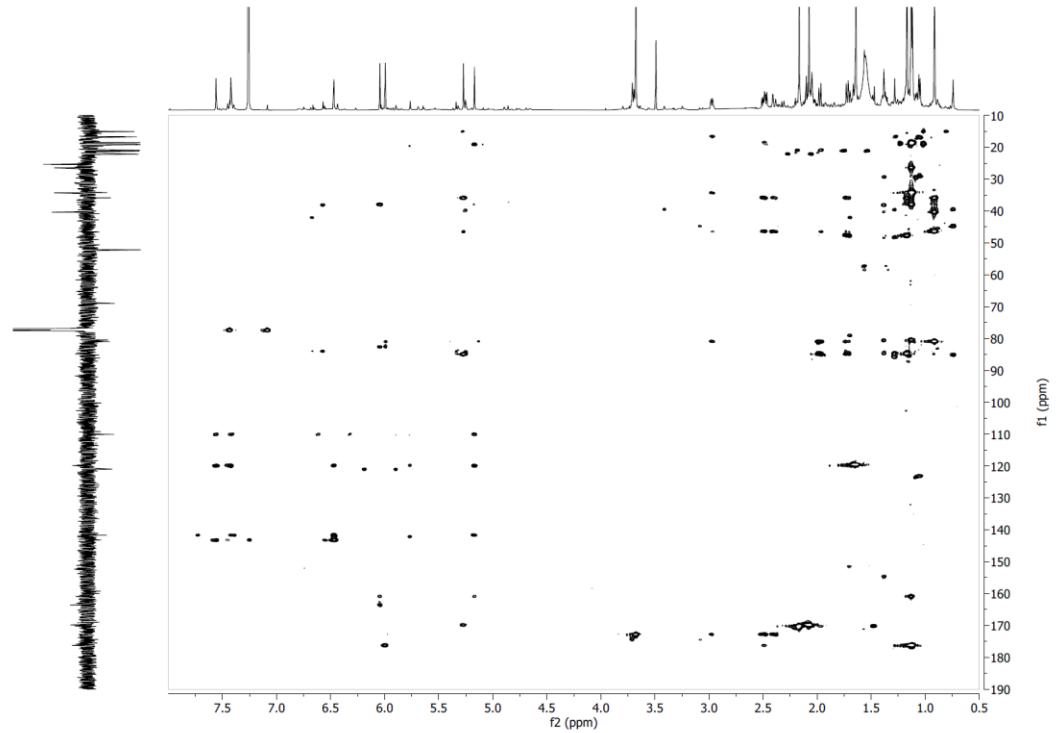
Supplementary Figure S4.2.110. COSY NMR spectrum of compound **19** in CDCl_3



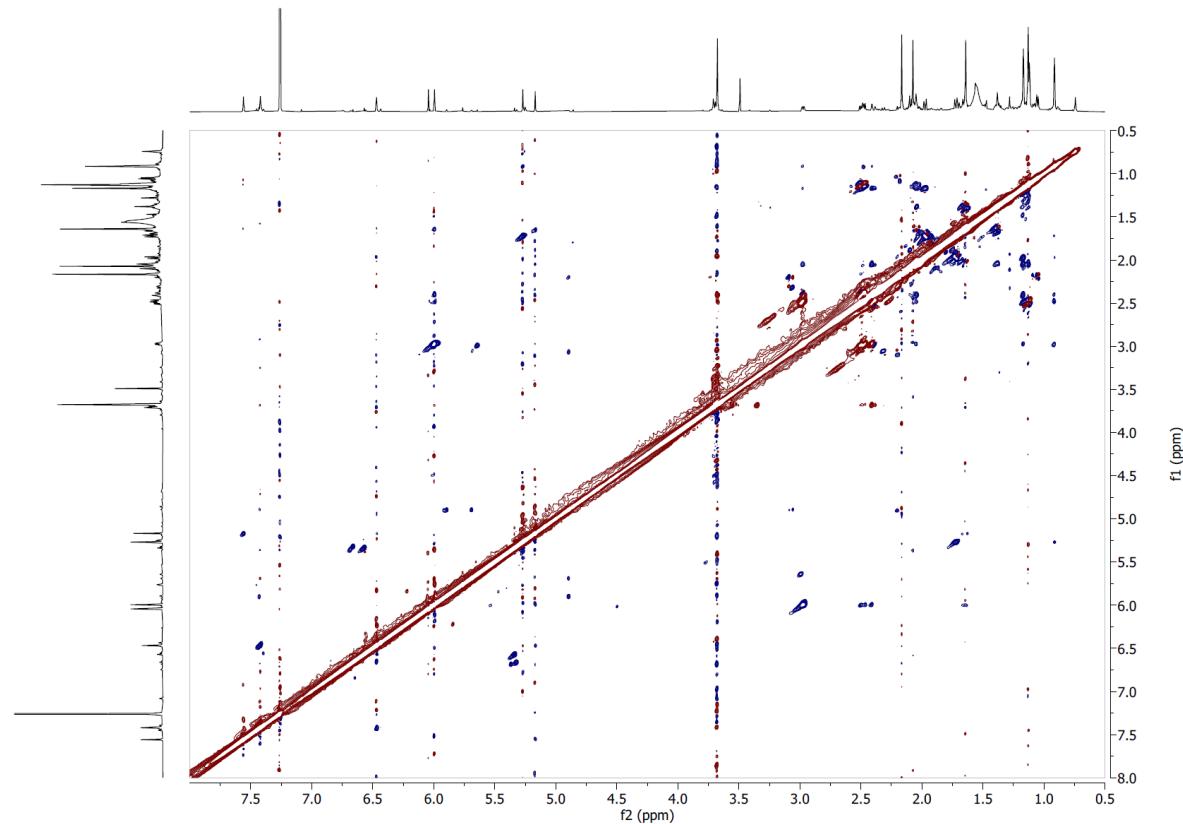
Supplementary Figure S4.2.111. ^{13}C -DEPTQ NMR spectrum of compound **19** in CDCl_3 at 151 MHz



Supplementary Figure S4.2.112. Edited HSQC NMR spectrum of compound **19** in CDCl_3

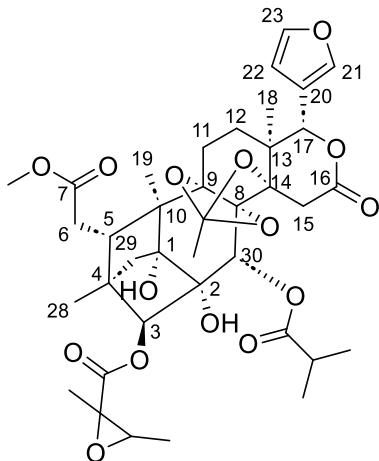


Supplementary Figure S4.2.113. HMBC NMR spectrum of compound **19** in CDCl_3



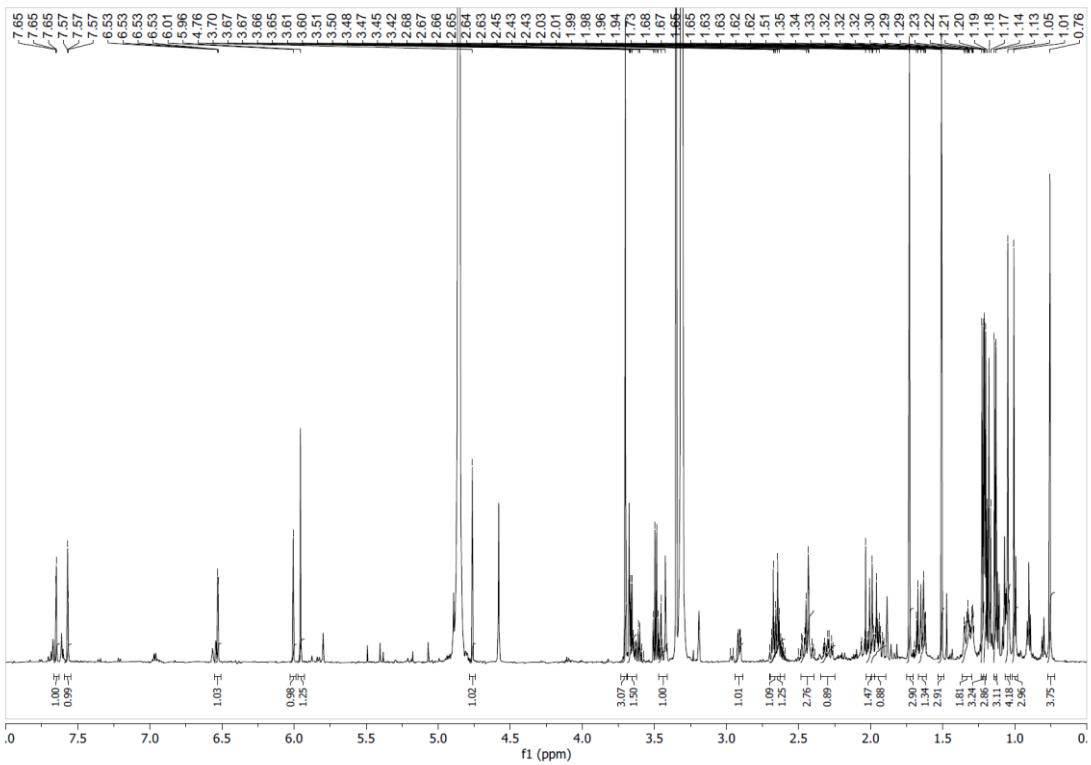
Supplementary Figure S4.2.114. ROESY NMR spectrum of compound **19** in CDCl_3

Compound 20. Amorphous white powder, HRESIMS m/z 745.3073 [M+H]⁺ (calculated for C₃₈H₄₉O₁₅, error 0.95 ppm), 743.2908 [M-H]⁻ (calculated for C₃₈H₄₇O₁₅, error -0.07 ppm); $[\alpha]_D^{20} -15$ (c 0.001 CHCl₃); UV (c 0.001, MeOH) λ_{max} 200, 235 nm.

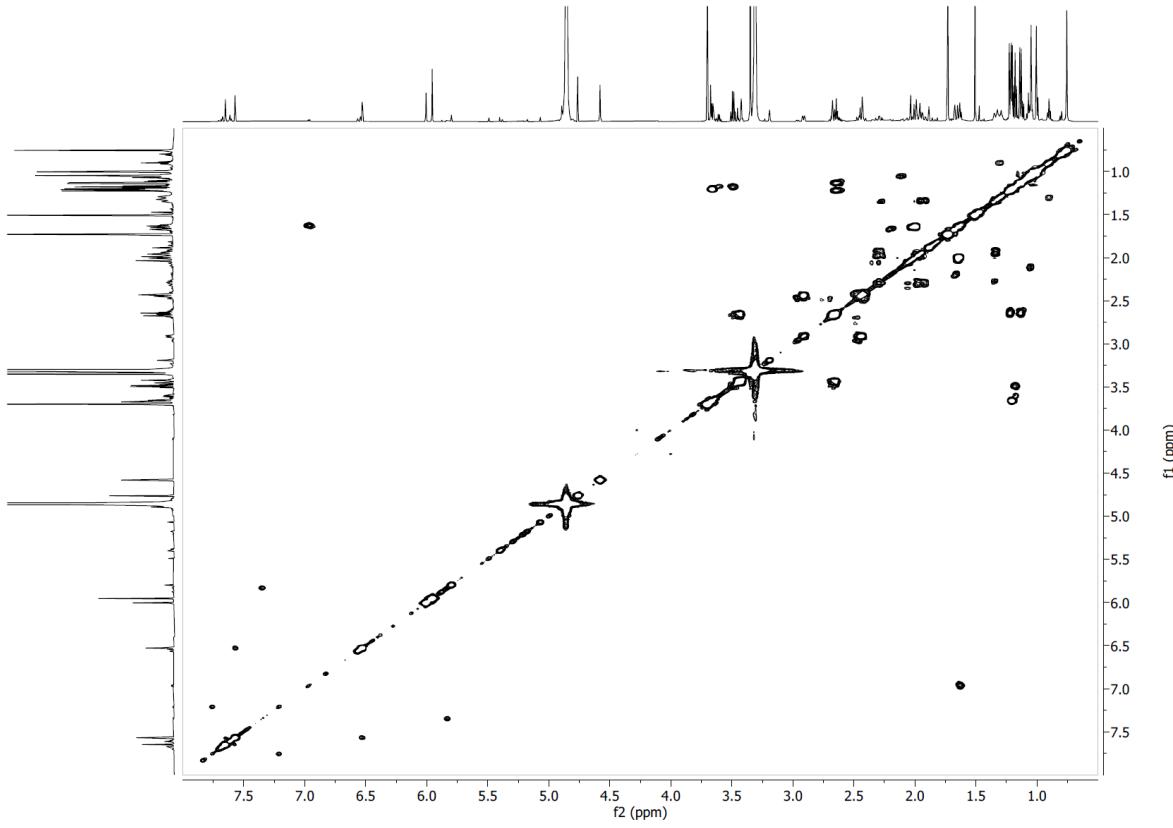


Chemical Formula: C₃₈H₄₈O₁₅
Exact Mass: 744.30

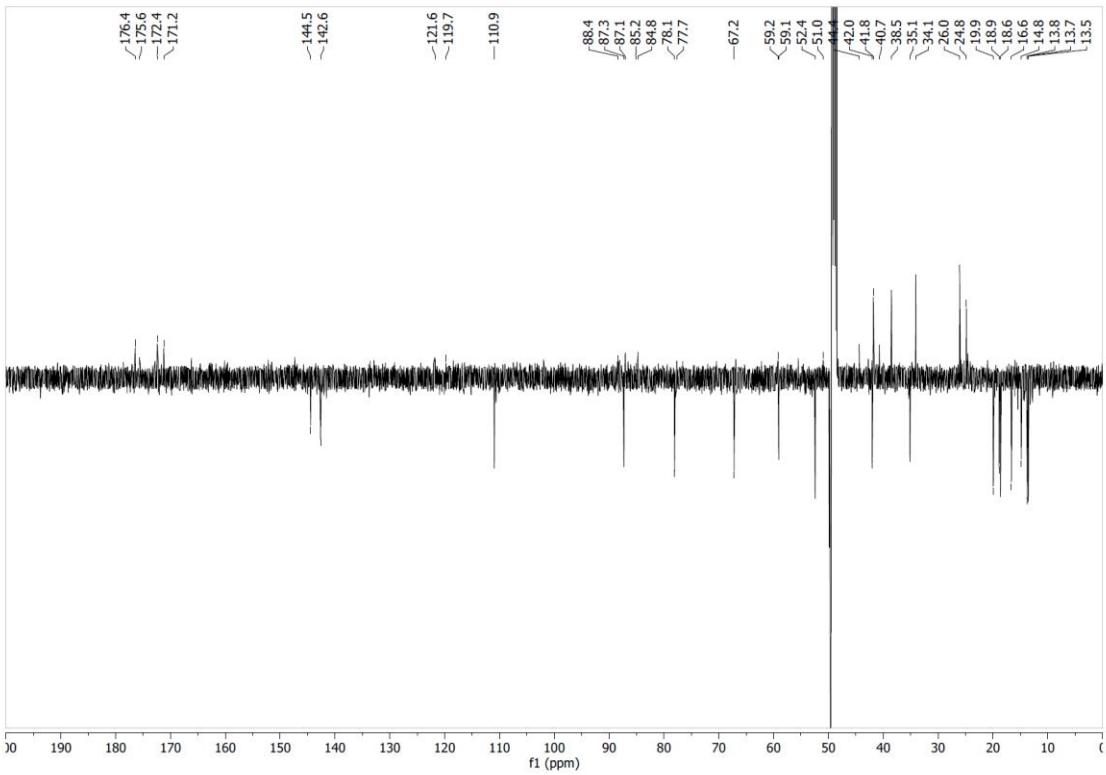
¹H NMR (CDCl₃, 600 MHz) δ 0.79 (3H, s, H₃-28), 1.02 (3H, s, H₃-18), 1.03 (3H, s, H₃-19), 1.14 (3H, d, J = 7.0 Hz, H₃-30d), 1.54 (3H, s, H₃-3e), 1.81 (1H, dt, J = 14.2, 4.3 Hz, H-11 α), 1.91 (1H, d, J = 11.5 Hz, H-29'), 2.21 (1H, d, J = 16.7 Hz, H-6''), 1.21 (3H, d, J = 5.4 Hz, H₃-3d), 1.21 (3H, d, J = 7.0 Hz, H₃-30c), 1.35 (1H, dt, J = 14.5, 4.3 Hz, H-12 β), 1.73 (1H, d, J = 11.5 Hz, H-29''), 1.76 (3H, s, H₃-34), 1.92 (1H, td, J = 14.5, 4.3 Hz, H-12 α), 1.81 (1H, dt, J = 14.2, 4.3 Hz, H-11 α), 2.30 (1H, td, J = 14.2, 4.3 Hz, H-11 β), 2.34 (1H, dd, J = 16.7, 11.0 Hz, H-6'), 2.57 (1H, d, J = 18.7 Hz, 15 β), 2.68 (1H, hept, J = 7.0 Hz, H-30b), 2.93 (1H, d, J = 11.0 Hz, H-5), 3.07 (1H, s, OH-2), 3.43 (1H, d, J = 18.7 Hz, H-15 α), 3.56 (1H, q, J = 5.4 Hz, H-3c), 3.68 (3H, s, OCH₃), 4.23 (1H, s, OH-1), 4.88 (1H, s, H-3), 5.90 (1H, s, H-30), 5.95 (1H, s, H-17), 6.44 (1H, d, J = 2.0 Hz, H-22), 7.43 (1H, d, J = 2.0 Hz, H-23), 7.58 (1H, s, H-21); ¹³C NMR (CDCl₃, 151 MHz) δ 13.5 (CH₃-3e), 13.5 (CH₃-3d), 13.8 (CH₃-19), 14.5 (CH₃-28), 16.8 (CH₃-34), 18.1 (CH₃-30d), 18.6 (CH₃-18), 19.9 (CH₃-30c), 24.0 (CH₂-11), 25.0 (CH₂-12), 33.7 (CH₂-6), 33.9 (CH-30b), 37.8 (CH₂-15), 39.6 (C-13), 40.9 (CH₂-29), 41.0 (CH-5), 43.6 (C-4), 49.9 (C-10), 52.2 (OCH₃), 58.0 (CH-3c), 58.2 (C-3b), 65.3 (CH-30), 75.7 (C-2), 76.3 (CH-17), 83.6 (C-1), 84.1 (C-14), 85.3 (CH-3), 85.7 (C-9), 87.6 (C-8), 110.0 (CH-22), 118.5 (C-33), 120.4 (C-20), 141.4 (CH-21), 143.0 (CH-23), 168.5 (C-16), 171.1 (C-3a), 173.4 (C-7), 174.7 (C-30a). Supplementary Figures S4.2.115–S4.2.120.



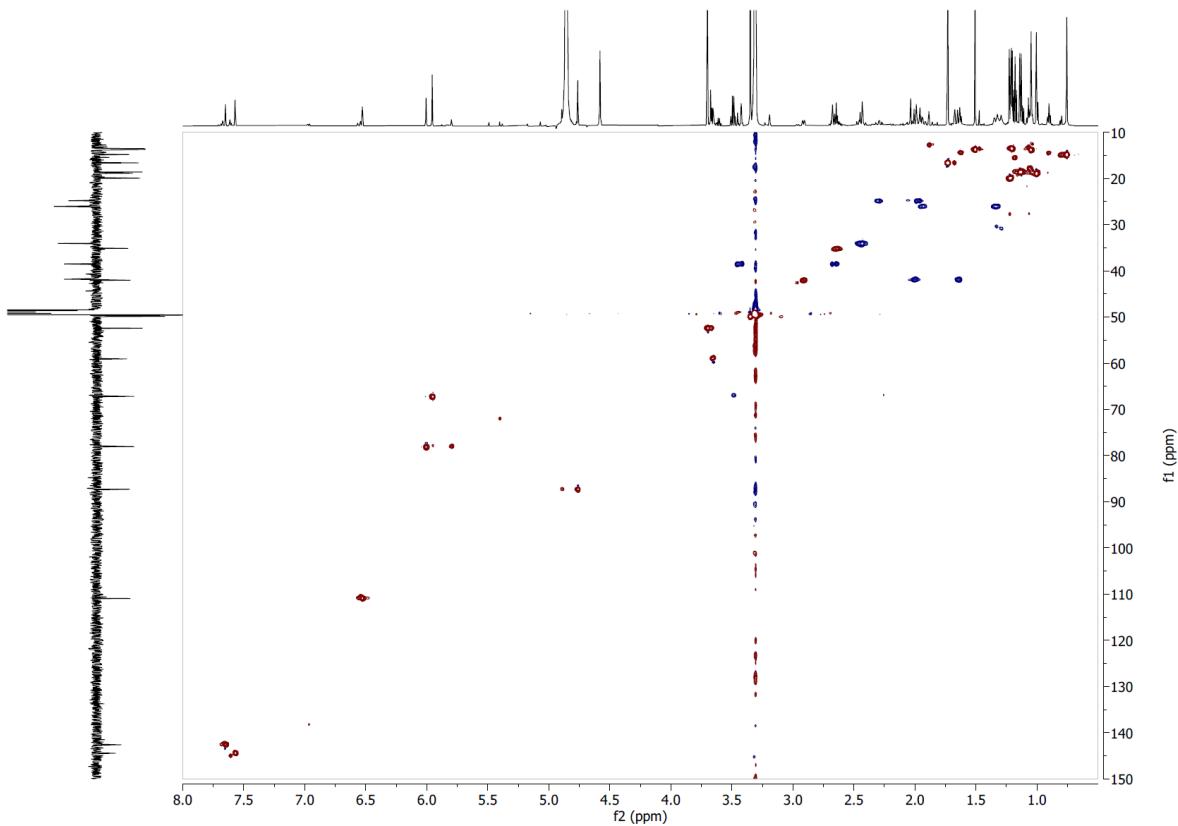
Supplementary Figure S4.2.115. ^1H NMR spectrum of compound **20** in CD_3OD at 600 MHz



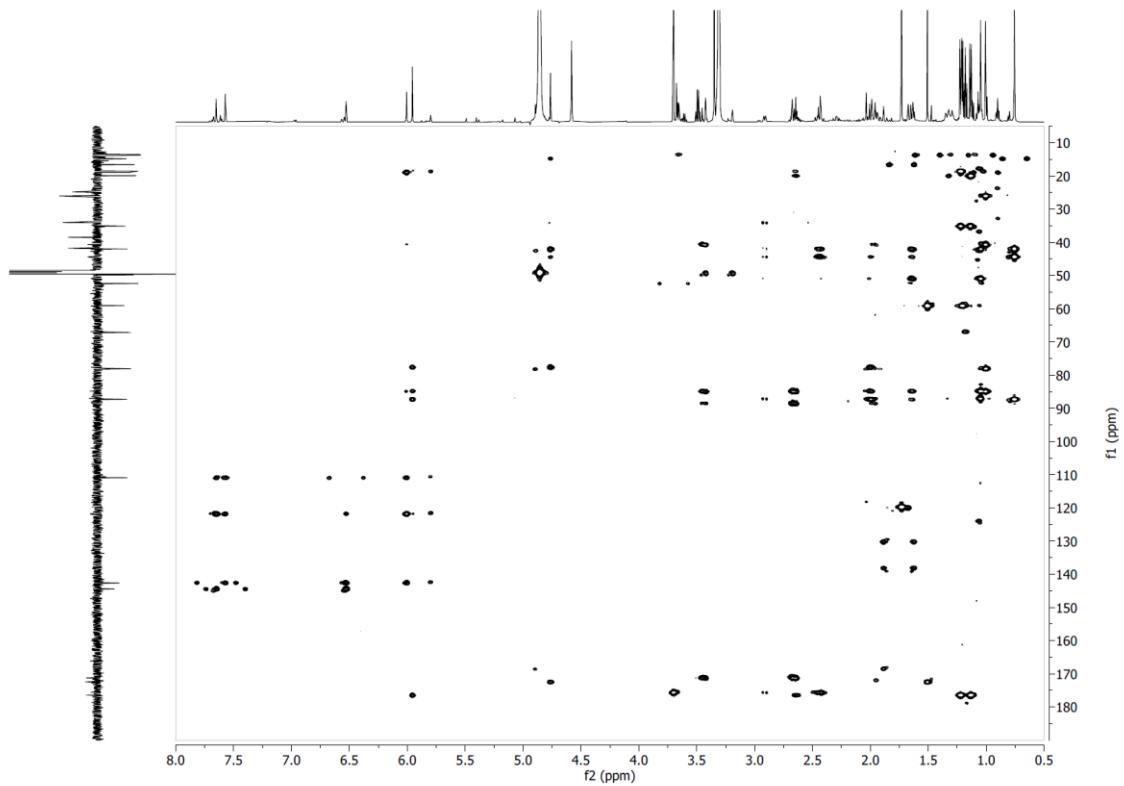
Supplementary Figure S4.2.116. COSY NMR spectrum of compound **21** in CD₃OD



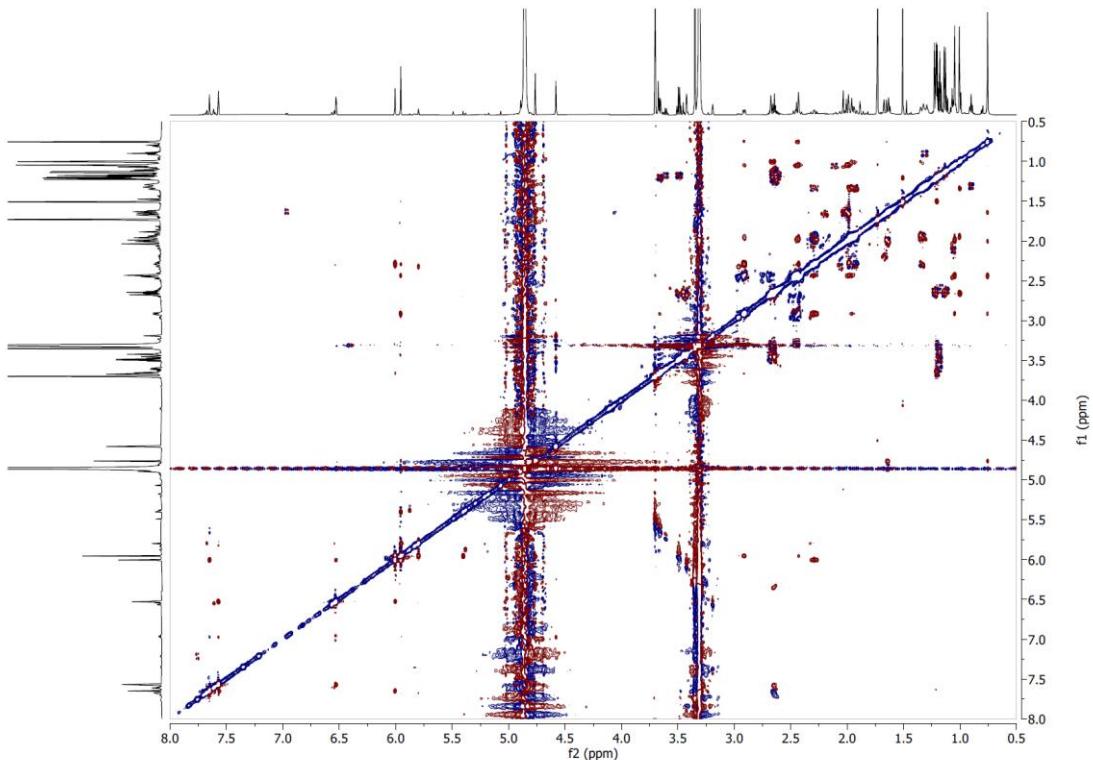
Supplementary Figure S4.2.117. ^{13}C -DEPTQ NMR spectrum of compound **22** in CD_3OD at 151 MHz



Supplementary Figure S4.2.118. Edited HSQC NMR spectrum of compound **23** in CD_3OD

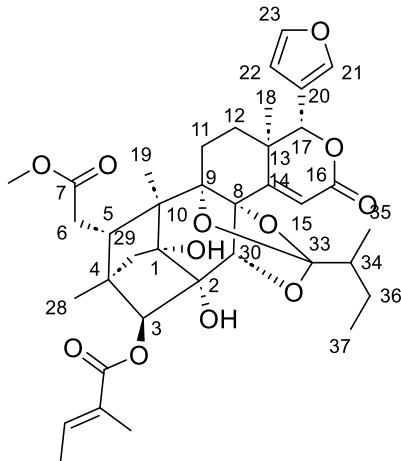


Supplementary Figure S4.2.119. HMBC NMR spectrum of compound **20** in CD₃OD



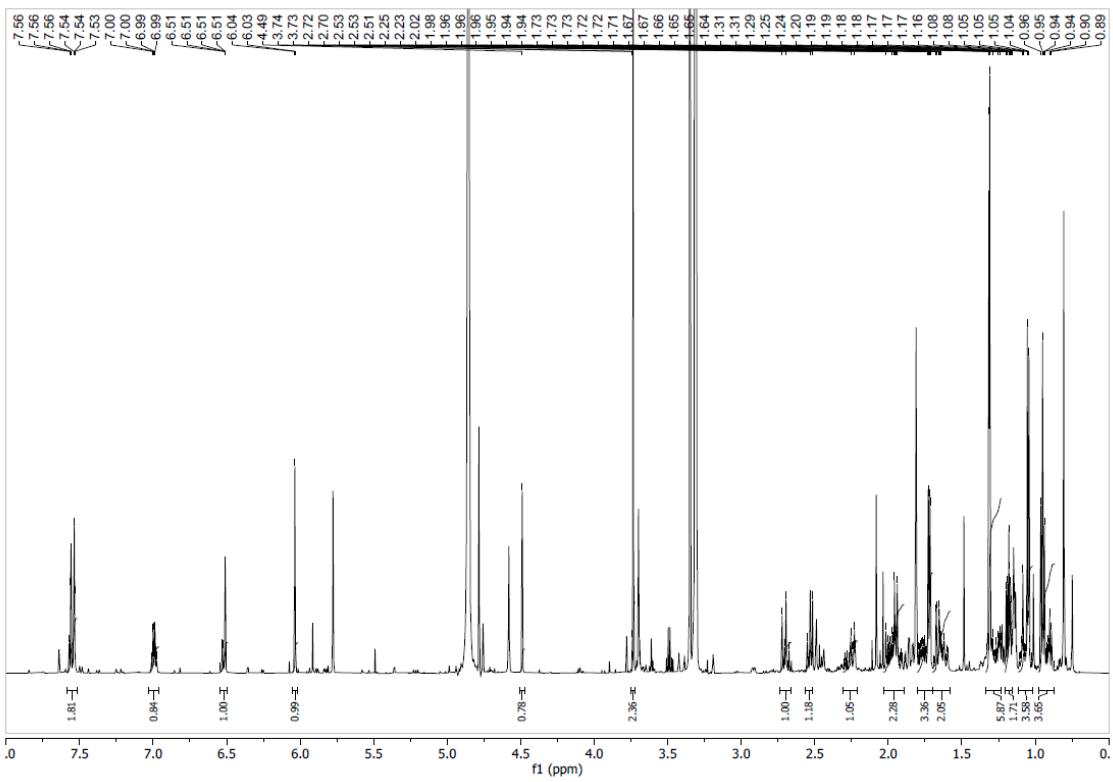
Supplementary Figure S4.2.120. ROESY NMR spectrum of compound **20** in CD₃OD

Compound 21: Swietephragmin C [60]. Amorphous white powder, HRESIMS m/z 683.3059 [$M+H$]⁺ (calculated for $C_{37}H_{47}O_{12}$, error -0.34 ppm), 681.2918 [$M-H$]⁻ (calculated for $C_{37}H_{45}O_{12}$, error 1.93 ppm); $[\alpha]_D^{20}$ 17 (c 0.0008 CHCl₃); UV (c 0.0008, MeOH) λ_{max} 216, 281 nm.

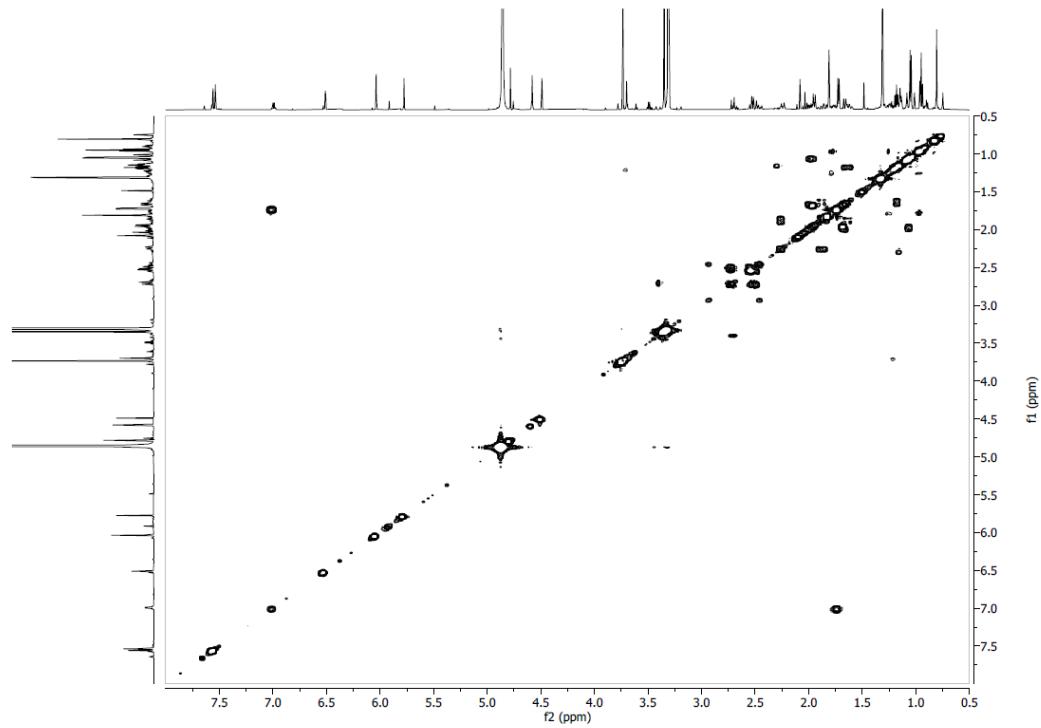


Chemical Formula: $C_{37}H_{46}O_{12}$
Exact Mass: 682.30

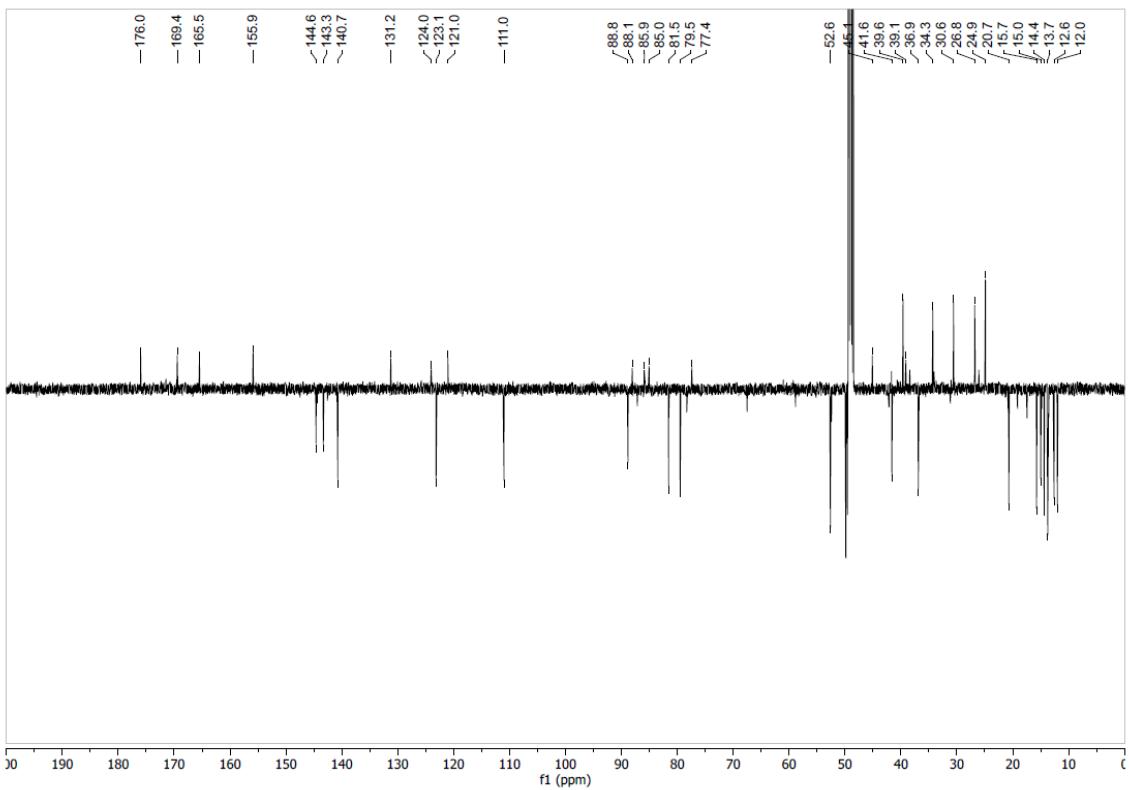
¹H NMR (CDCl₃, 600 MHz) δ 0.82 (3H, s, H₃-28), 0.92 (3H, t, J = 7.5 Hz, H₃-37), 1.02 (3H, d, J = 6.8 Hz, H₃-35), 1.12 (1H, dt, J = 14.0, 3.6 Hz, H-12 α), 1.22 (1H, m, H-36 $''$), 1.28 (3H, s, H₃-19), 1.33 (3H, s, H₃-18), 1.51 (1H, td, J = 14.0, 3.6 Hz, H-12 β), 1.70 (1H, m, H-36 $''$), 1.75 (3H, d, J = 7.0 Hz, H₃-3d), 1.78 (1H, d, J = 12.0 Hz, H-29 $''$), 1.82 (1H, d, J = 12.0 Hz, H-29 $''$), 1.85 (3H, s, H₃-3e), 1.86 (1H, td, J = 15.0, 3.4 Hz, H-11 α), 1.92 (1H, m, H-34), 2.08 (1H, dt, J = 15.0, 3.4 Hz, H-11 β), 2.38 (1H, dd, J = 16.5, 11.5 Hz, H-6 $''$), 2.43 (1H, d, J = 16.5 Hz, H-6 $''$), 2.55 (1H, d, J = 11.5 Hz, H-5), 3.49 (1H, s, OH-1), 3.72 (3H, s, OCH₃), 4.49 (1H, s, H-30), 4.83 (1H, s, H-3), 5.68 (1H, s, H-17), 5.97 (1H, s, H-15), 6.44 (1H, t, J = 1.7 Hz, H-22), 6.91 (1H, q, J = 7.0 Hz, H-3c), 7.42 (1H, t, J = 1.7 Hz, H-23), 7.47 (1H, d, J = 1.7 Hz, H-21); ¹³C NMR (CDCl₃, 151 MHz) δ 11.8 (CH₃-37), 12.6 (CH₃-3e), 13.5 (CH₃-35), 14.6 (CH₃-3d), 14.8 (CH₃-28), 15.8 (CH₃-19), 20.1 (CH₃-18), 23.9 (CH₂-36), 26.0 (CH₂-11), 29.3 (CH₂-12), 34.0 (CH₂-6), 35.8 (CH-34), 38.0 (C-13), 38.9 (CH₂-29), 40.4 (CH-5), 44.0 (C-4), 47.5 (C-10), 52.3 (OCH₃), 75.9 (C-2), 78.1 (CH-30), 79.9 (CH-17), 83.8 (C-8), 84.8 (C-1), 86.7 (C-9), 86.8 (CH-3), 110.2 (CH-22), 119.9 (C-20), 122.6 (CH-15), 122.8 (C-33), 130.1 (C-3b), 140.0 (CH-3c), 142.0 (CH-21), 143.2 (CH-23), 153.0 (C-14), 163.1 (C-16), 168.1 (C-3a), 173.8 (C-7). Supplementary Figures S4.2.121-S4.2.126.



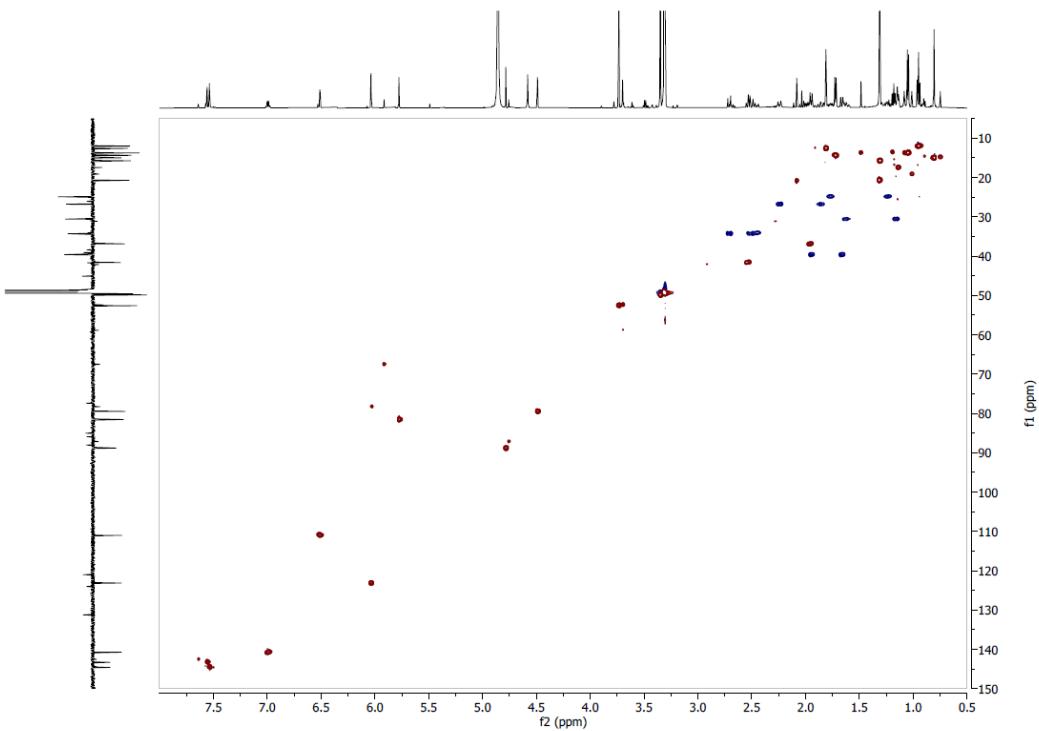
Supplementary Figure S4.2.121. ^1H NMR spectrum of compound **21** in CD_3OD at 600 MHz



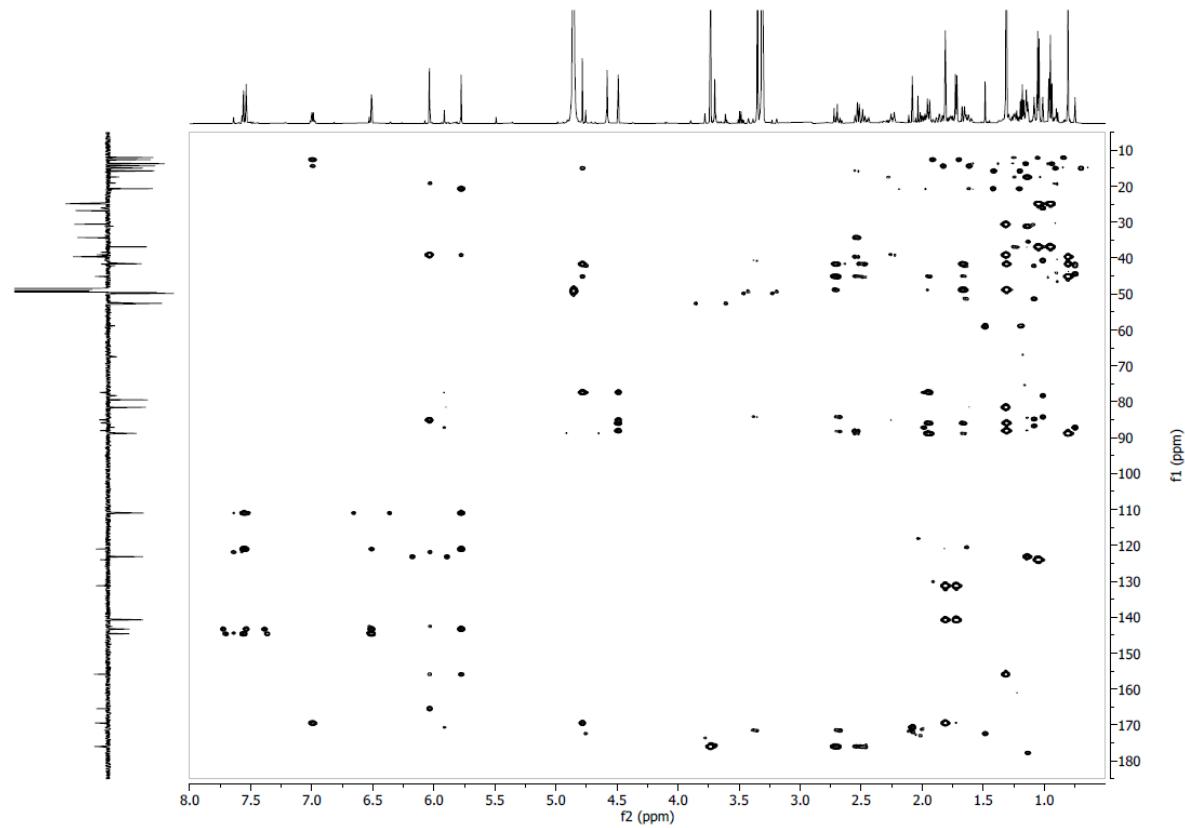
Supplementary Figure S4.2.122. COSY NMR spectrum of compound **21** in CD_3OD



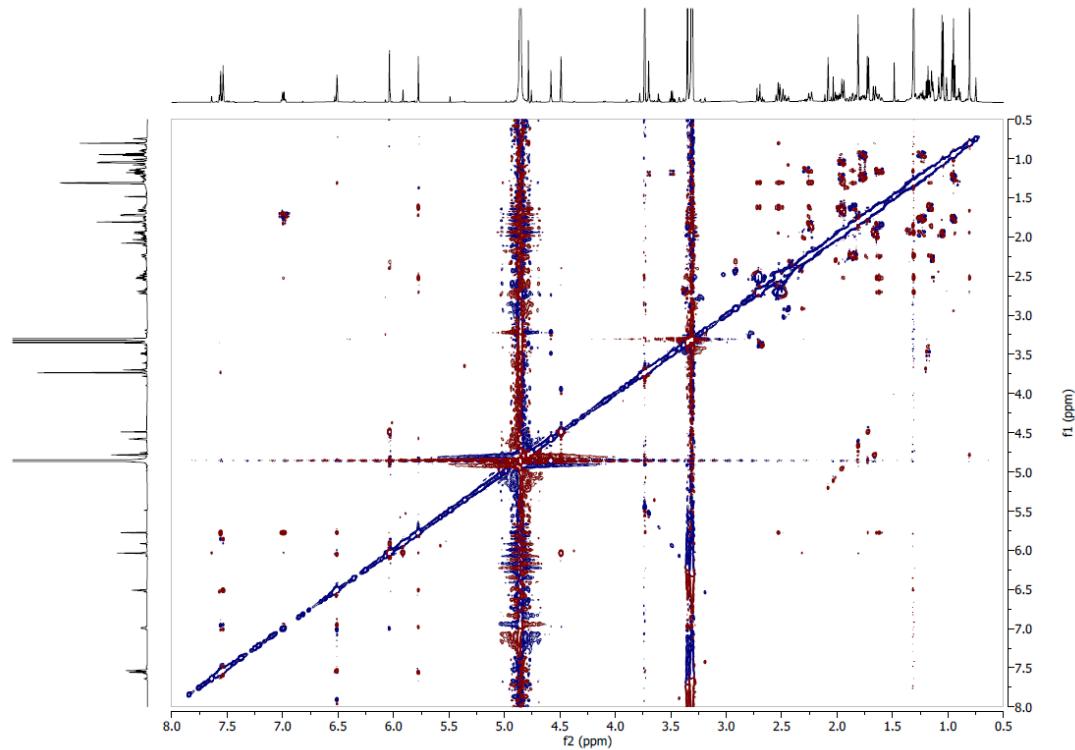
Supplementary Figure S4.2.123. ^{13}C -DEPTQ NMR spectrum of compound **21** in CD_3OD at 151 MHz



Supplementary Figure S4.2.124. Edited HSQC NMR spectrum of compound **21** in CD_3OD

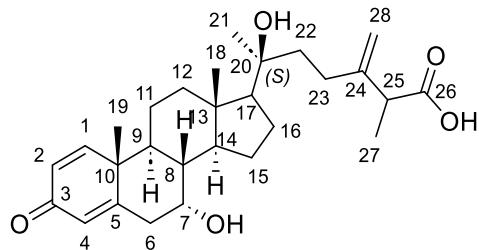


Supplementary Figure S4.2.125. HMBC NMR spectrum of compound **21** in CD_3OD



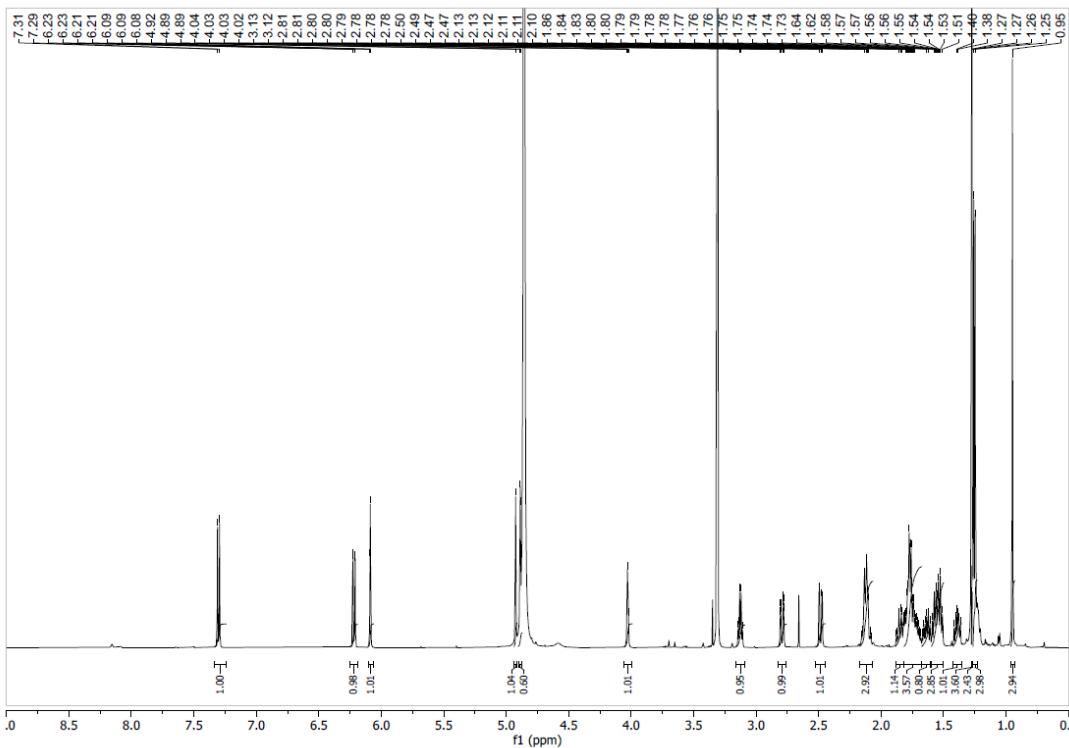
Supplementary Figure S4.2.126. ROESY NMR spectrum of compound **21** in CD_3OD

Compound 22: 7,20-dihydroxy-3-oxo-ergosta-1,4,24-trien-26-oic acid. Amorphous white powder, HRESIMS m/z 427.3221 [M+H]⁺ (calculated for C₂₈H₄₃O₃, error -0.04 ppm); $[\alpha]_D^{20} -5$ (c 0.003 CHCl₃); UV (c 0.003, CHCl₃) λ_{max} 210, 251 nm.

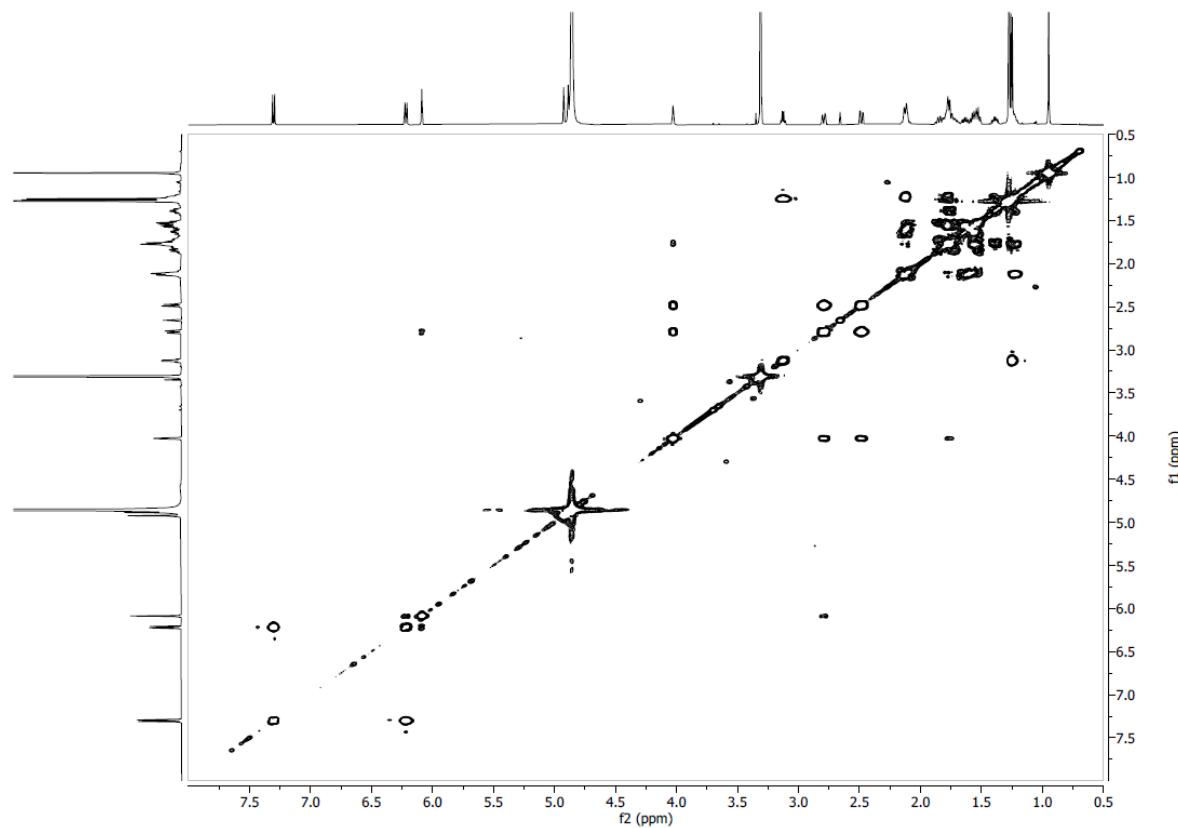


¹H NMR (CD₃OD, 600 MHz) δ 0.95 (3H, s, H₃-18), 1.23 (1H, m, H-12a), 1.25 (3H, d, $J = 7.0$ Hz, H₃-27), 1.25 (1H, m, H-15¹¹), 1.27 (3H, s, H₃-21), 1.27 (3H, s, H₃-19), 1.39 (1H, ddd, $J = 12.9, 11.1, 6.8$ Hz, H-14), 1.52 (1H, m, H-17), 1.55 (1H, m, H-9), 1.57 (1H, m, H-22¹¹), 1.63 (1H, m, H-22¹), 1.72 (1H, m, H-16a), 1.76 (1H, m, H-8), 1.78 (2H, m, H₂-11), 1.80 (1H, m, H-15¹), 1.85 (1H, dt, $J = 12.9, 10.9, 2.3$ Hz, 16 β), 2.12 (3H, m, H₂-23, H-12b), 2.48 (1H, dd, $J = 13.7, 3.1$ Hz, H-6 α), 2.79 (1H, dt, $J = 13.7, 3.1, 1.8$ Hz, H-6 β), 3.13 (1H, q, $J = 7.0$ Hz, H-25), 4.03 (1H, q, $J = 3.1$ Hz, H-7), 4.89 (1H, s, H-28¹¹), 4.92 (1H, s, H-28¹), 6.09 (1H, t, $J = 1.8$ Hz, H-4), 6.22 (1H, dd, $J = 10.1, 1.8$ Hz, H-2), 7.30 (1H, d, $J = 10.1$ Hz, H-1); ¹³C NMR (CD₃OD, 151 MHz) δ 14.0 (CH₃-18), 17.0 (CH₃-27), 18.8 (CH₃-19), 23.4 (CH₂-16), 23.6 (CH₂-11), 24.2 (CH₂-15), 25.9 (CH₂-21), 30.5 (CH₂-23), 40.3 (CH-8), 41.0 (CH-12), 42.2 (CH₂-6), 43.3 (CH₂-22), 44.0 (C-13), 45.4 (C-10), 45.7 (CH-9), 47.0 (CH-25), 51.7 (CH-14), 59.5 (CH-17), 70.5 (CH-7), 75.6 (C-20), 111.0 (CH₂-28), 126.9 (CH-4), 127.6 (CH-2), 150.6 (C-24), 159.5 (CH-1), 170.1 (C-5), 178.3 (C-26), 188.3 (C-3).

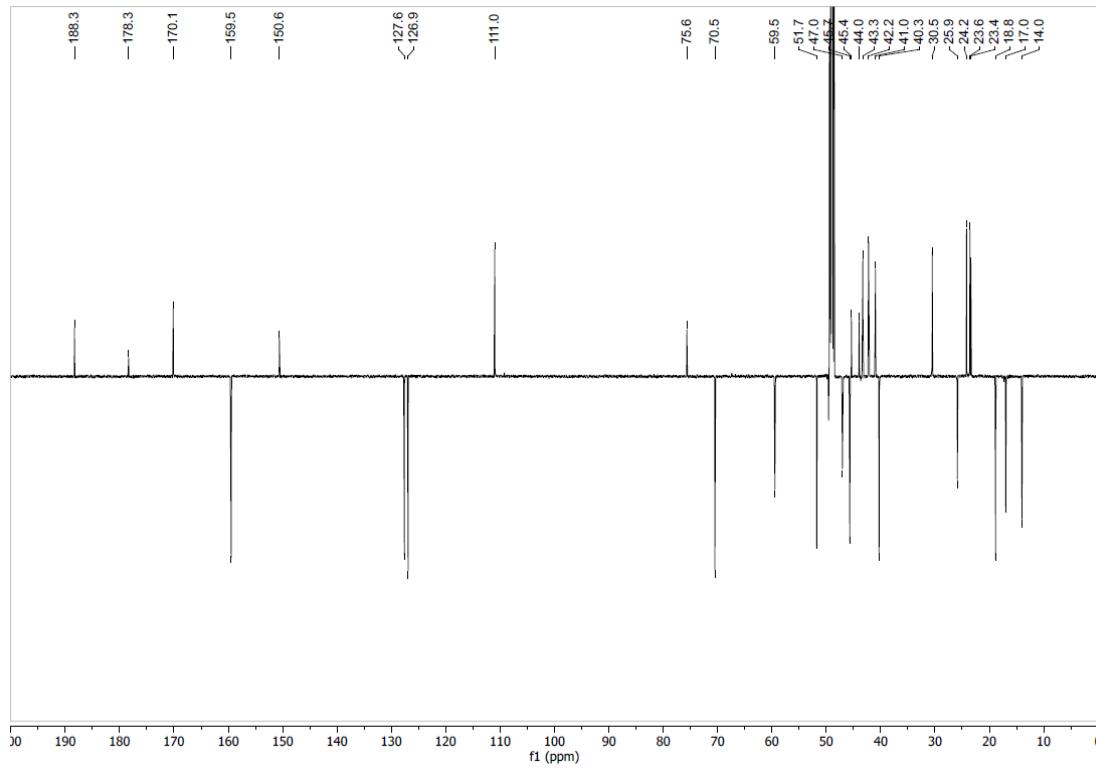
Supplementary Figures S4.2.127-S4.2.132.



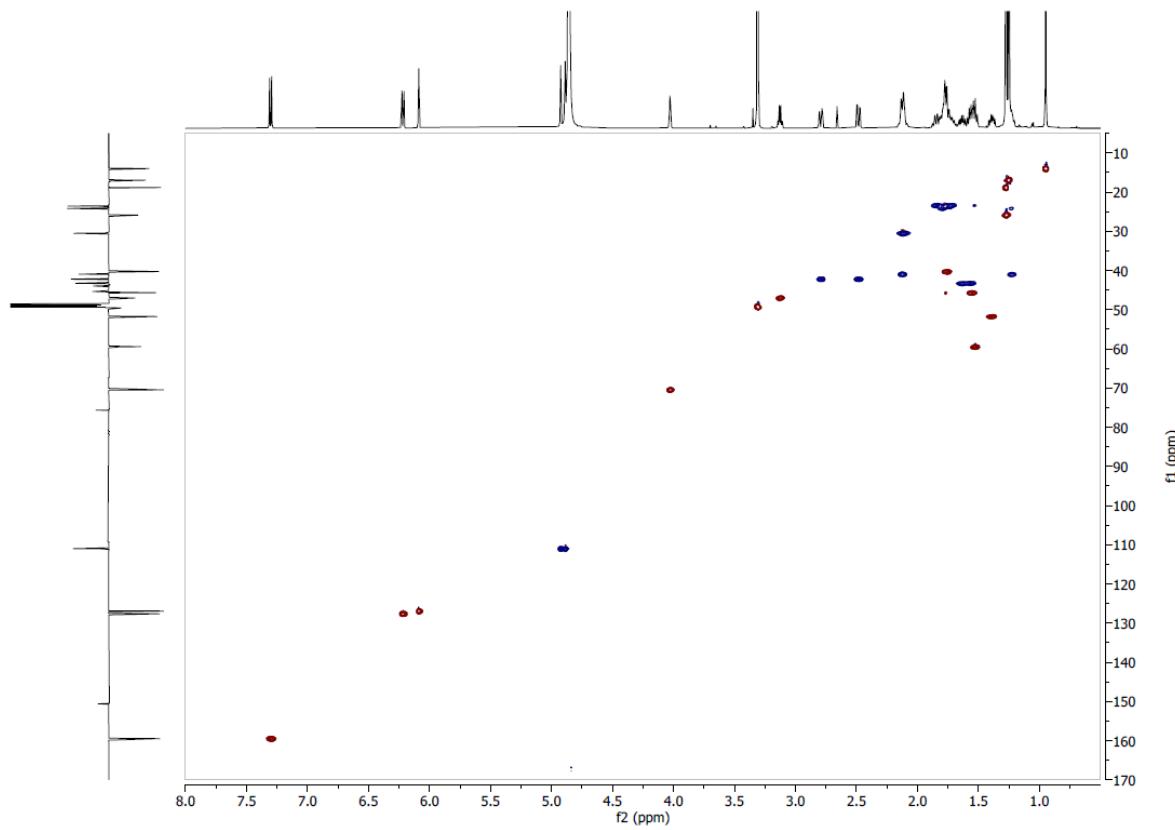
Supplementary Figure S4.2.127. ^1H NMR spectrum of compound **22** in CD_3OD at 600 MHz



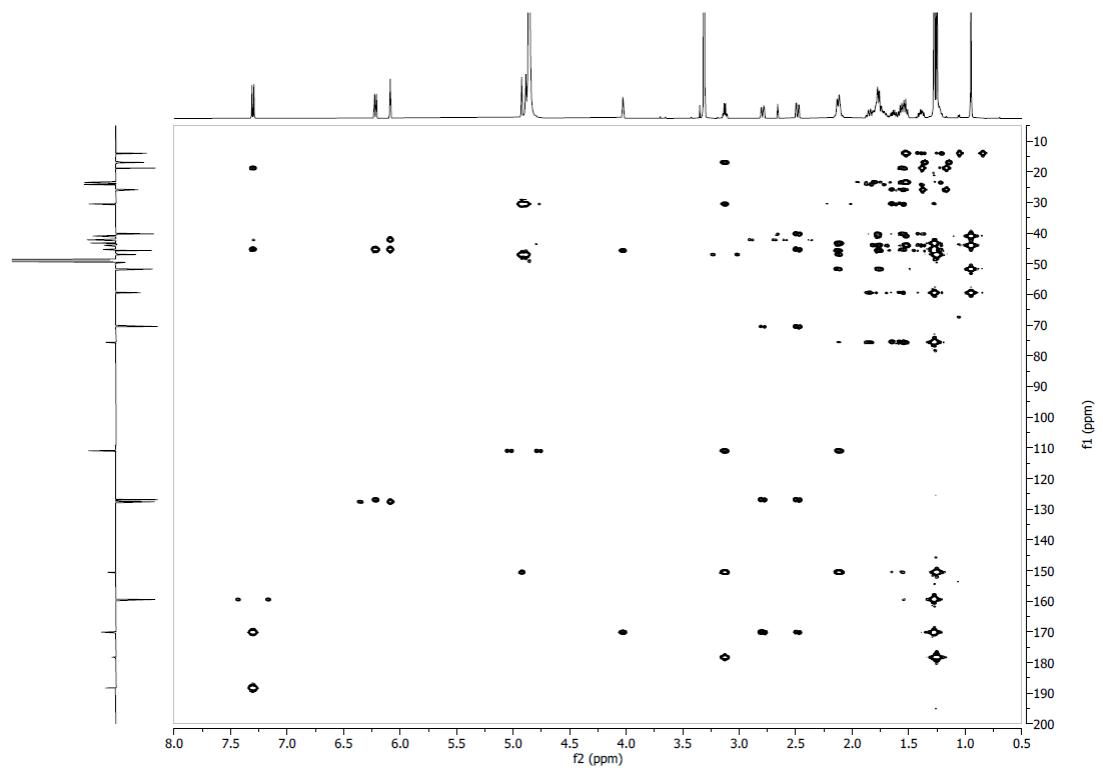
Supplementary Figure S4.2.128. COSY NMR spectrum of compound **22** in CD_3OD



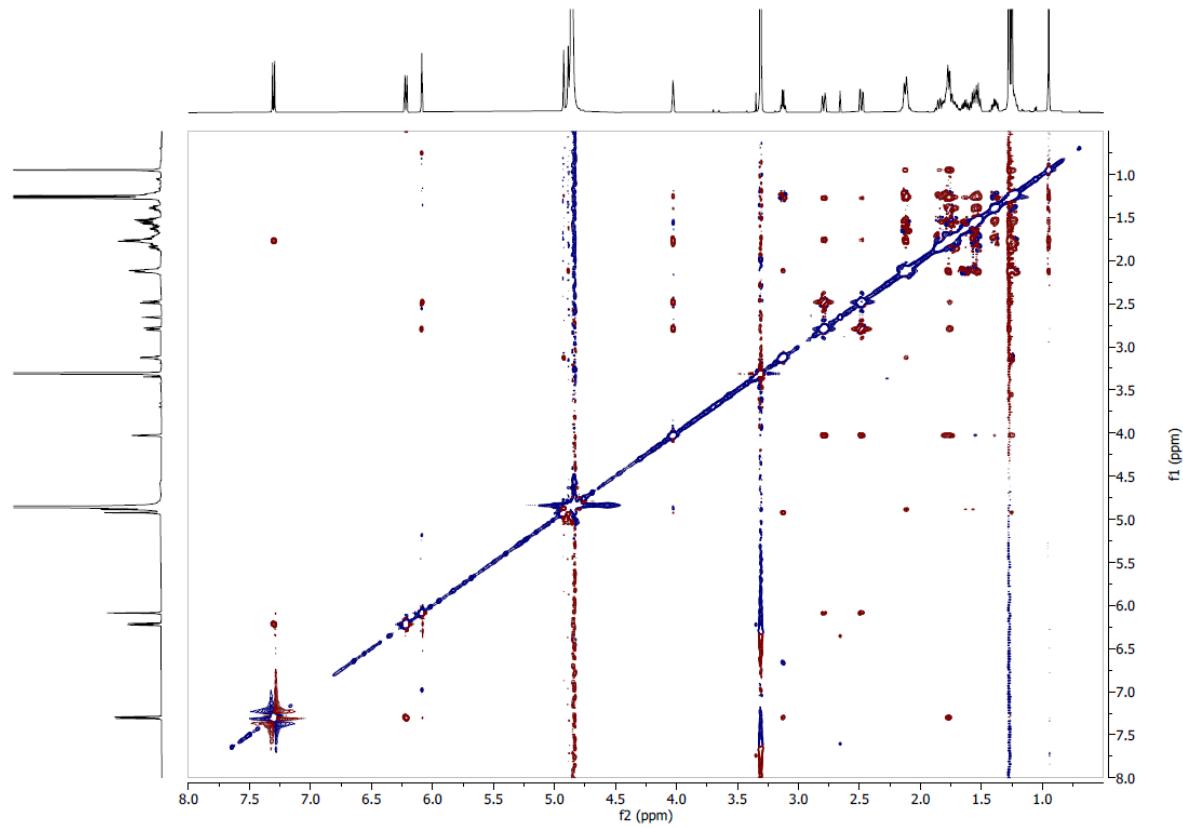
Supplementary Figure S4.2.129. ^{13}C -DEPTQ NMR spectrum of compound **22** in CD_3OD at 151 MHz



Supplementary Figure S4.2.130. Edited HSQC NMR spectrum of compound **22** in CD_3OD

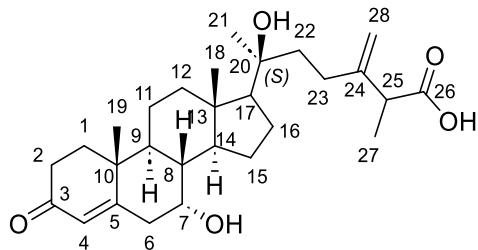


Supplementary Figure S4.2.131. HMBC NMR spectrum of compound **22** in CD_3OD

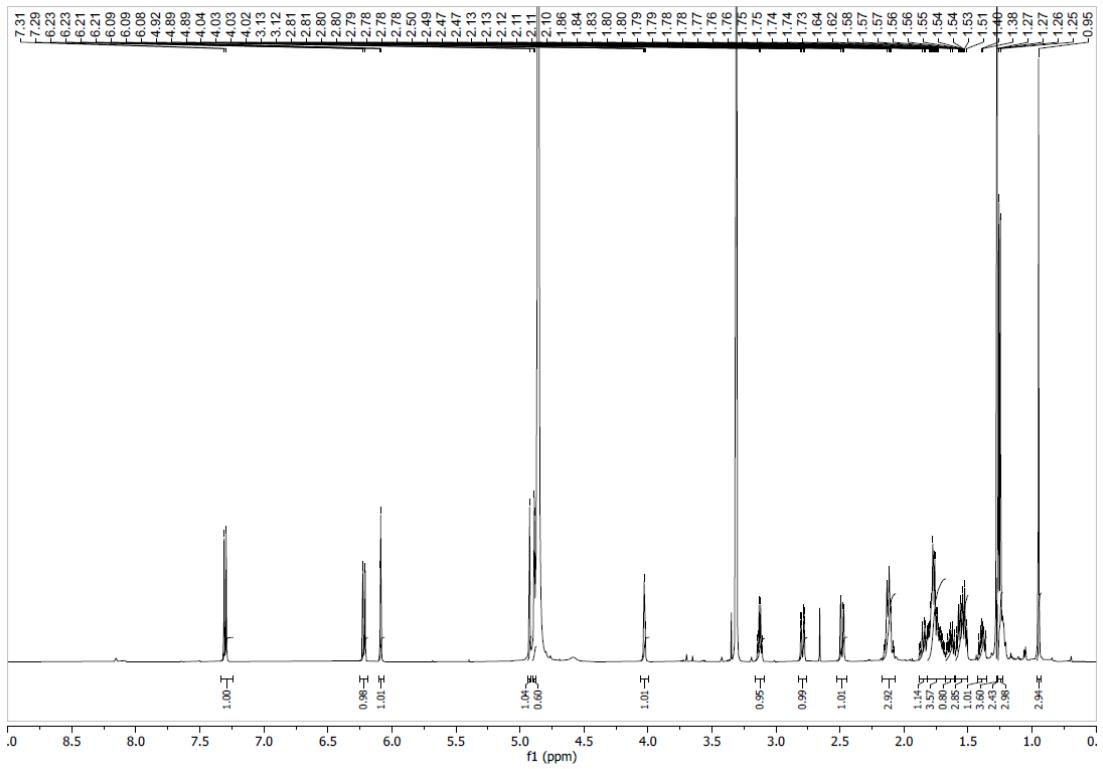


Supplementary Figure S4.2.132. ROESY NMR spectrum of compound **22** in CD_3OD

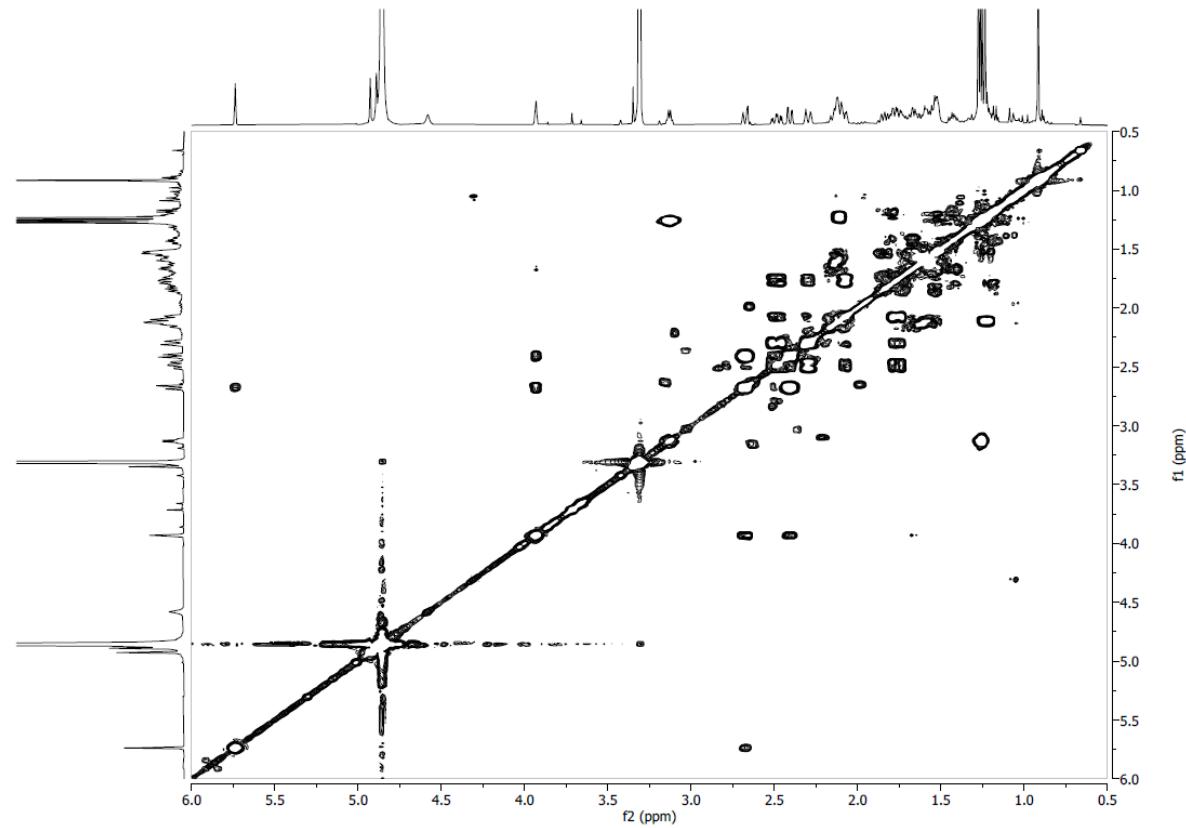
Compound **23**: 7,20-dihydroxy-3-oxo-ergosta-4,24-dien-26-oic acid. Amorphous white powder, HRESIMS m/z 459.3095 [M+H]⁺ (calculated for C₃₈H₄₃O₅, error -1.09 ppm); $[\alpha]_D^{20} +1$ (c 0.0008 CHCl₃); UV (c 0.0008, CHCl₃) λ_{max} 205, 242 nm.



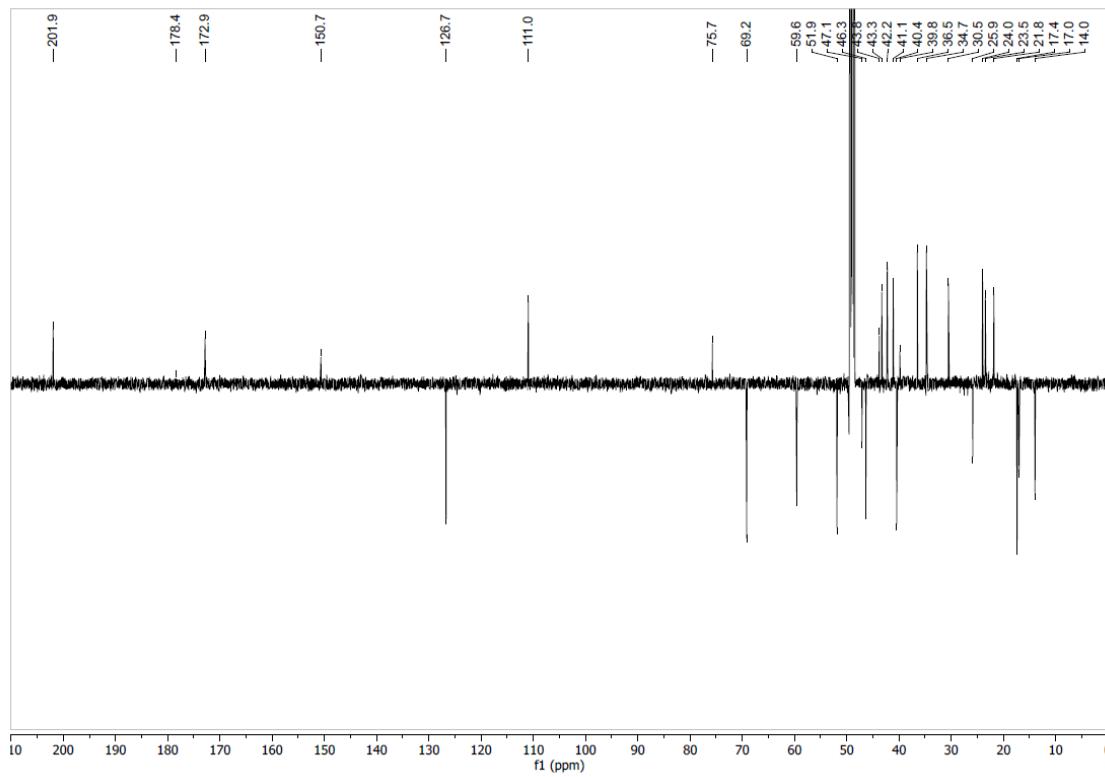
¹H NMR (CD₃OD, 600 MHz) δ 0.92 (3H, s, H₃-18), 1.21 (1H, m, H-15¹¹), 1.22 (1H, m, H-12a), 1.24 (3H, s, H₃-19), 1.26 (3H, d, J = 7.1 Hz, H₃-27), 1.27 (3H, s, H₃-21), 1.43 (1H, td, J = 12.0, 6.9 Hz, H-14), 1.52 (1H, m, H-9), 1.53 (1H, m, H-11b), 1.54 (1H, m, H-17), 1.58 (1H, m, H-22¹¹), 1.60 (1H, m, H-11a), 1.63 (1H, m, H-22'), 1.67 (1H, m, H-8), 1.74 (1H, m, H-16¹¹), 1.77 (1H, m, H-1a), 1.79 (1H, m, H-15'), 1.84 (1H, m, H-16'), 2.08 (1H, m, H-1b), 2.11 (1H, m, H-12b), 2.13 (2H, m, H₂-23), 2.30 (1H, dt, J = 17.0, 3.7 Hz, H-2a), 2.41 (1H, dd, J = 15.0, 3.0 Hz, H-6a), 2.49 (1H, td, J = 17.0, 14.8, 5.1 Hz, H-2b), 2.68 (1H, dt, J = 15.0, 3.0, 2.0 Hz, H-6b), 3.13 (1H, q, J = 7.1 Hz, H-25), 3.93 (1H, q, J = 3.0 Hz, H-7), 4.89 (1H, s, H-28¹¹), 4.93 (1H, s, H-28'), 5.74 (1H, d, J = 2.0 Hz, H-4); ¹³C NMR (CD₃OD, 151 MHz) δ 14.0 (CH₃-18), 17.0 (CH₃-27), 17.4 (CH₃-19), 21.8 (CH₂-11), 23.5 (CH₂-16), 24.0 (CH₂-15), 25.9 (CH₂-21), 30.5 (CH₂-23), 34.7 (CH₂-2), 36.5 (CH₂-1), 39.8 (C-10), 40.4 (CH-8), 41.1 (CH₂-12), 42.2 (CH₂-6), 43.3 (CH₂-22), 43.8 (C-13), 46.3 (CH-9), 47.1 (CH-25), 51.9 (CH-14), 59.6 (CH-17), 69.2 (CH-7), 75.7 (C-20), 111.0 (CH₂-28), 126.7 (CH-4), 150.7 (C-24), 172.9 (C-5), 178.4 (C-26), 201.9 (C-3). Supplementary Figures S4.2.133-S4.2.138.



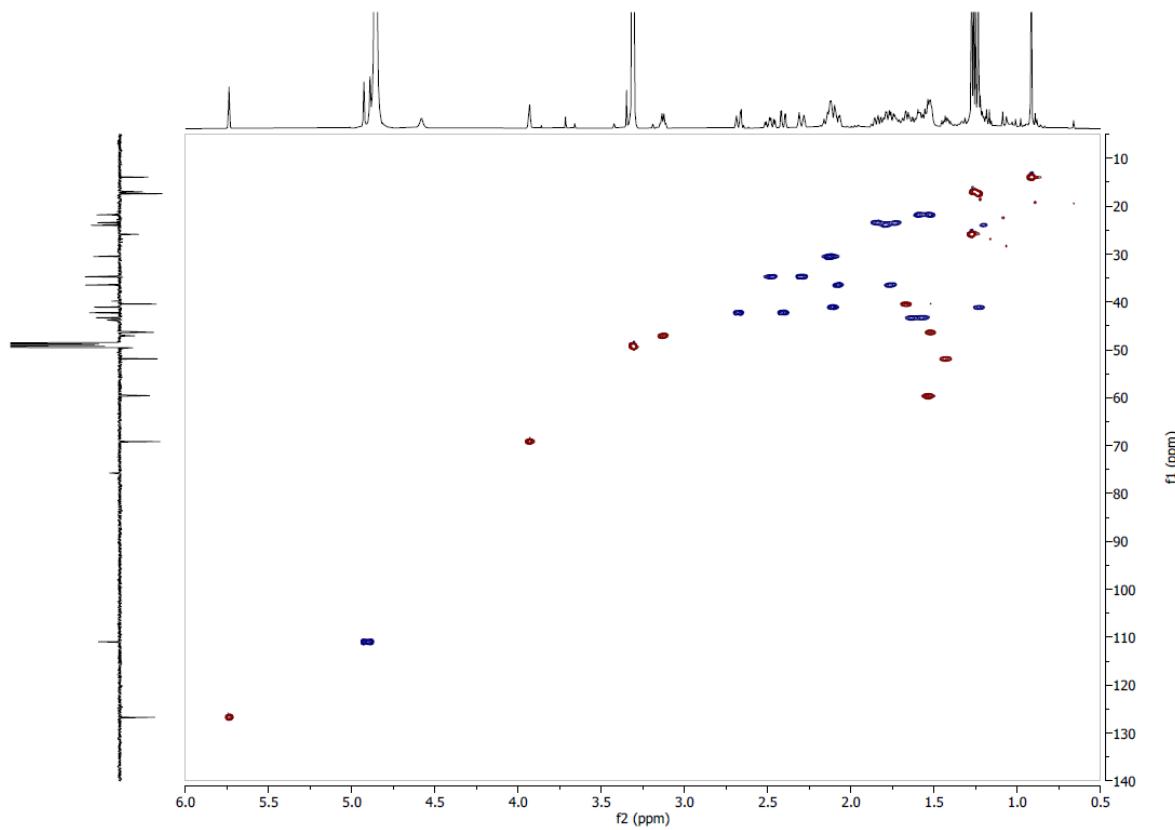
Supplementary Figure S4.2.1323. ¹H NMR spectrum of compound **23** in CD_3OD



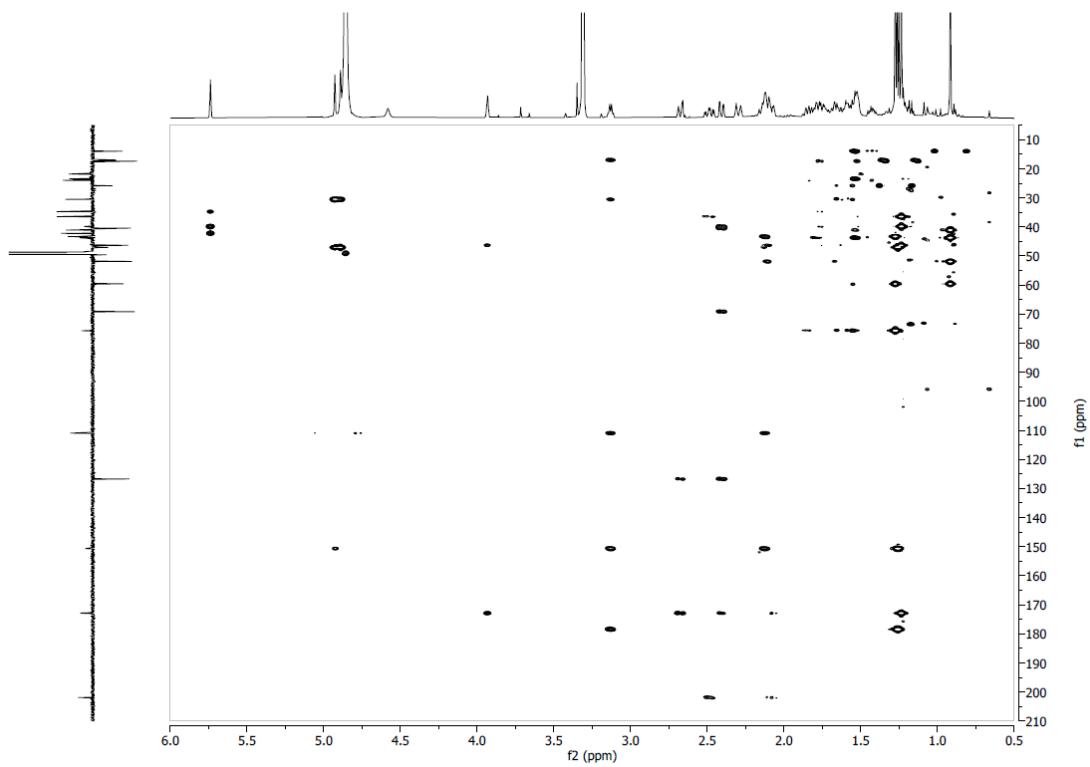
Supplementary Figure S4.2.134. COSY NMR spectrum of compound **23** in CD_3OD



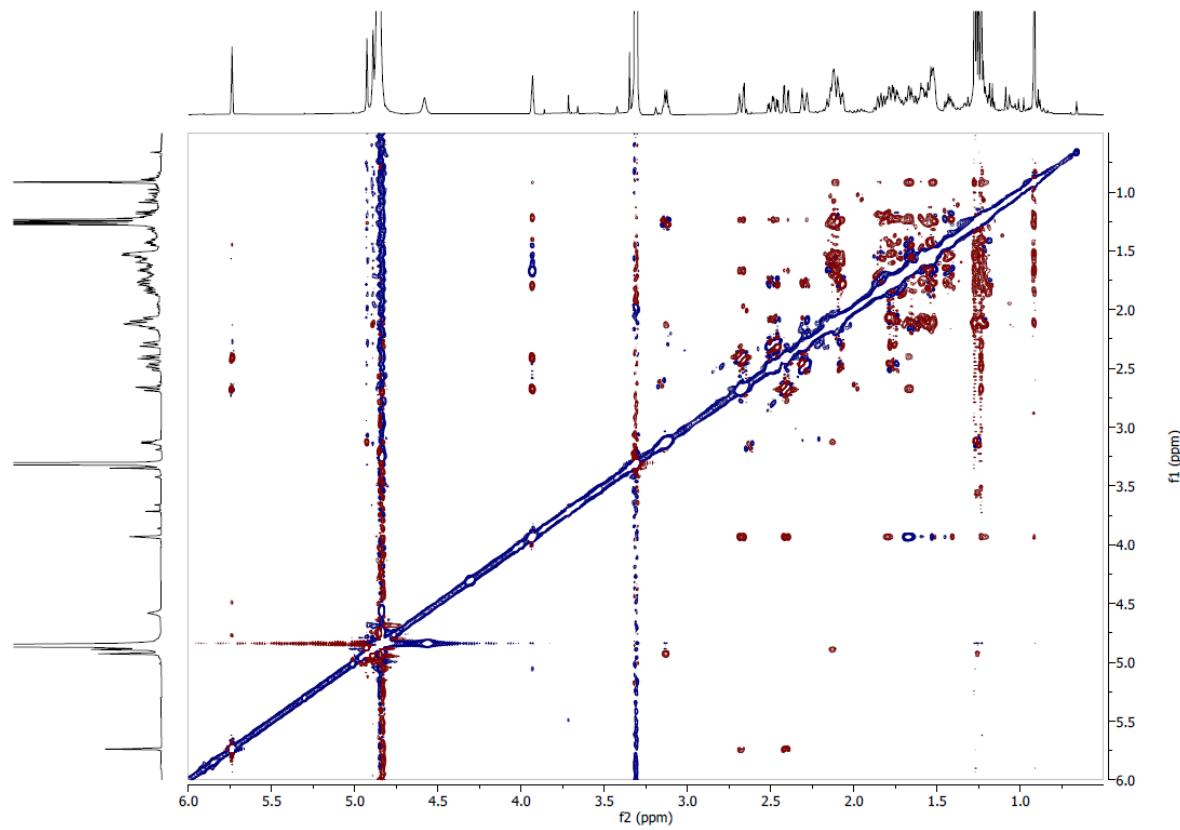
Supplementary Figure S4.2.135. ^{13}C -DEPTQ NMR spectrum of compound **23** in CD_3OD at 151 MHz



Supplementary Figure S4.2.136. Edited HSQC NMR spectrum of compound **23** in CD_3OD

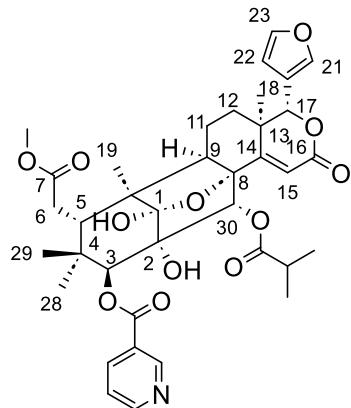


Supplementary Figure S4.2.137. HMBC NMR spectrum of compound **23** in CD_3OD

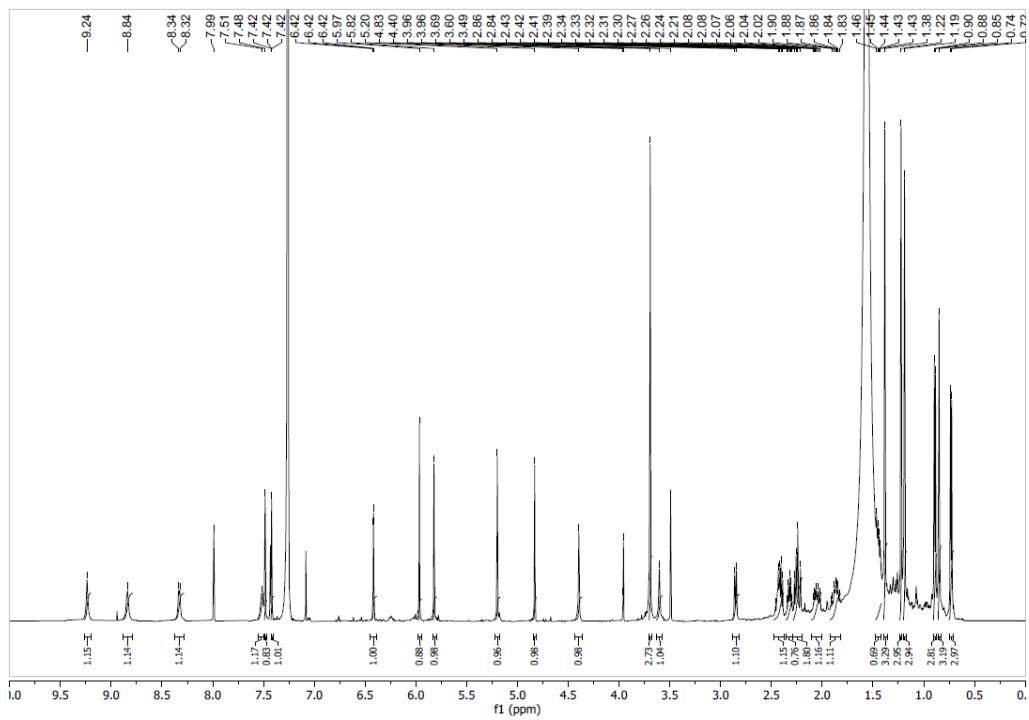


Supplementary Figure S4.2.138. ROESY NMR spectrum of compound **23** in CD_3OD

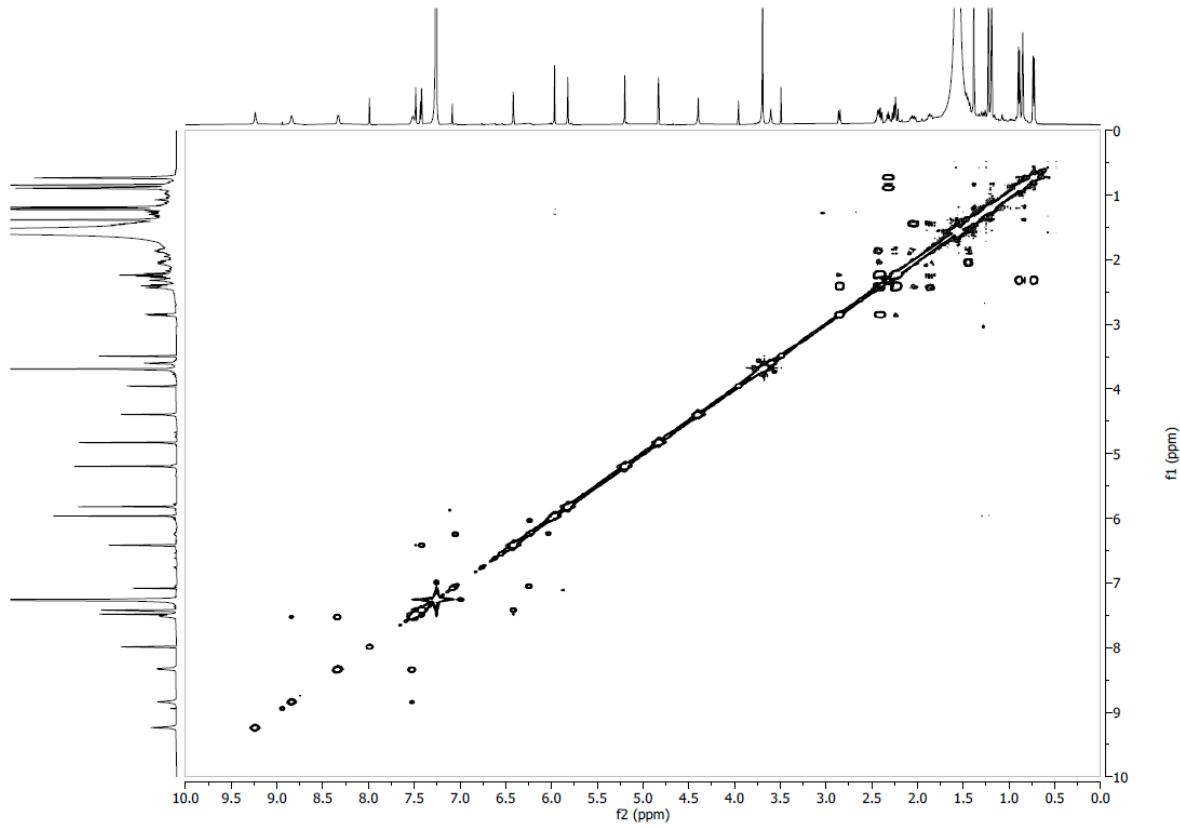
Compound 24: Entanutilin B [84]. Amorphous white powder, HRESIMS m/z 694.2868 [$M+H$]⁺ (calculated for C₃₇H₄₄NO₁₂, error 1.43 ppm); $[\alpha]_D^{20} -28$ (c 0.0003 CHCl₃); UV (c 0.003, CHCl₃) λ_{max} 198 nm.



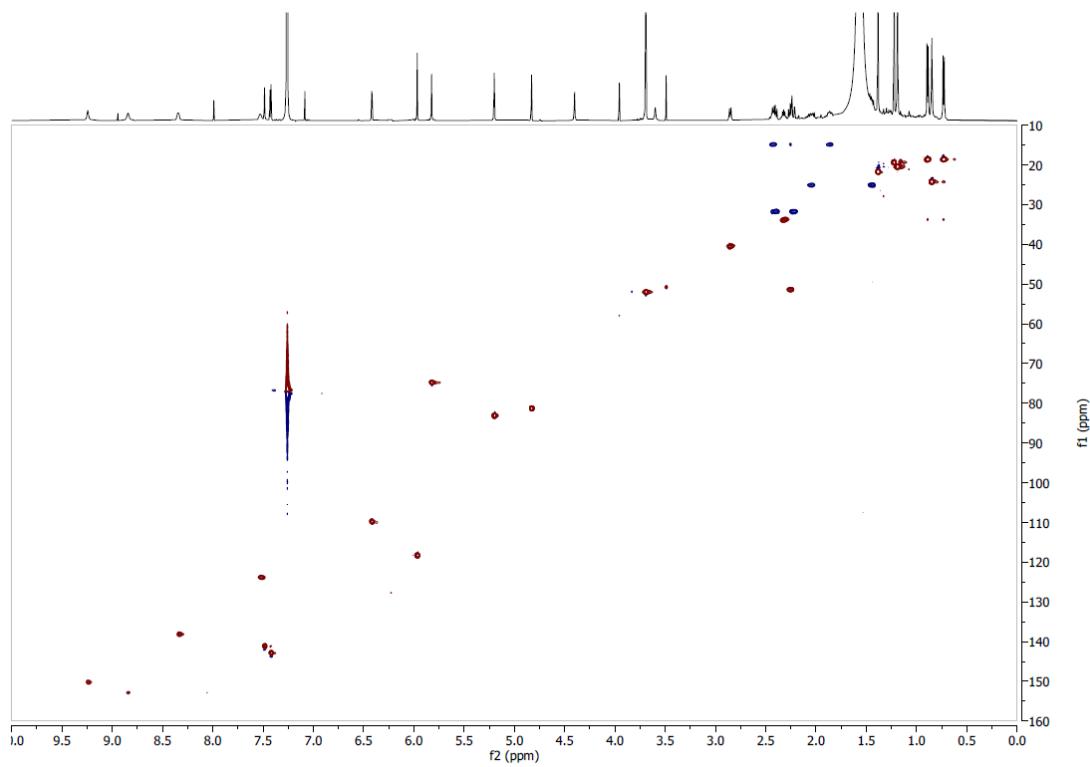
¹H NMR (CDCl₃, 600 MHz) δ 0.73 (3H, d, J = 6.9 Hz, H₃-30d), 0.85 (3H, s, H₃-29b), 0.89 (3H, d, J = 6.9 Hz, H₃-30c), 1.19 (3H, s, H₃-19), 1.22 (3H, s, H₃-18), 1.38 (3H, s, H₃-28a), 1.44 (1H, m, 12a), 1.87 (1H, m, 11a), 2.05 (1H, m, 12b), 2.25 (2H, m, H-6'', H-9), 2.32 (1H, hept, J = 6.9 Hz, H-30b), 2.41 (2H, m, H-6', H-11b), 2.85 (1H, d, J = 10.0 Hz, H-5), 3.60 (1H, s, OH-2), 3.69 (3H, s, OCH₃), 4.40 (1H, s, OH-1), 4.83 (1H, s, H-17), 5.20 (1H, s, H-3), 5.82 (1H, s, H-30), 5.97 (1H, s, H-15), 6.42 (1H, t, J = 1.6 Hz, H-22), 7.42 (1H, t, J = 1.6 Hz, H-23), 7.48 (1H, s, H-21), 7.51 (1H, brs, H-3e), 8.33 (1H, d, J = 7.5 Hz, H-3f), 8.84 (1H, s, H-3d), 9.24 (1H, s, H-3c); ¹³C NMR (CDCl₃, 151 MHz) δ 14.8 (CH₂-11), 18.5 (CH₃-30d), 18.7 (CH₃-30c), 19.4 (CH₃-18), 20.5 (CH₃-19), 21.7 (CH₃-28a), 24.2 (CH₃-29b), 25.0 (CH₂-12), 31.7 (CH₂-6), 33.9 (CH-30b), 38.7 (C-4), 38.9 (C-13), 40.5 (CH-5), 42.3 (C-10), 51.4 (CH-9), 51.9 (OCH₃), 74.7 (CH-30), 80.2 (C-8), 80.9 (C-2), 81.3 (CH-17), 83.1 (CH-3), 108.1 (C-1), 109.8 (CH-22), 118.2 (CH-15), 119.8 (C-20), 123.9 (CH-3e), 138.1 (CH-3f), 141.1 (CH-21), 142.8 (CH-23), 150.2 (CH-3c), 152.9 (CH-3d), 158.2 (C-14), 162.9 (C-16), 164.5 (C3a), 173.7 (C-7), 174.8 (C-30a). **Supplementary Figures S4.2.139-S4.2.143.**



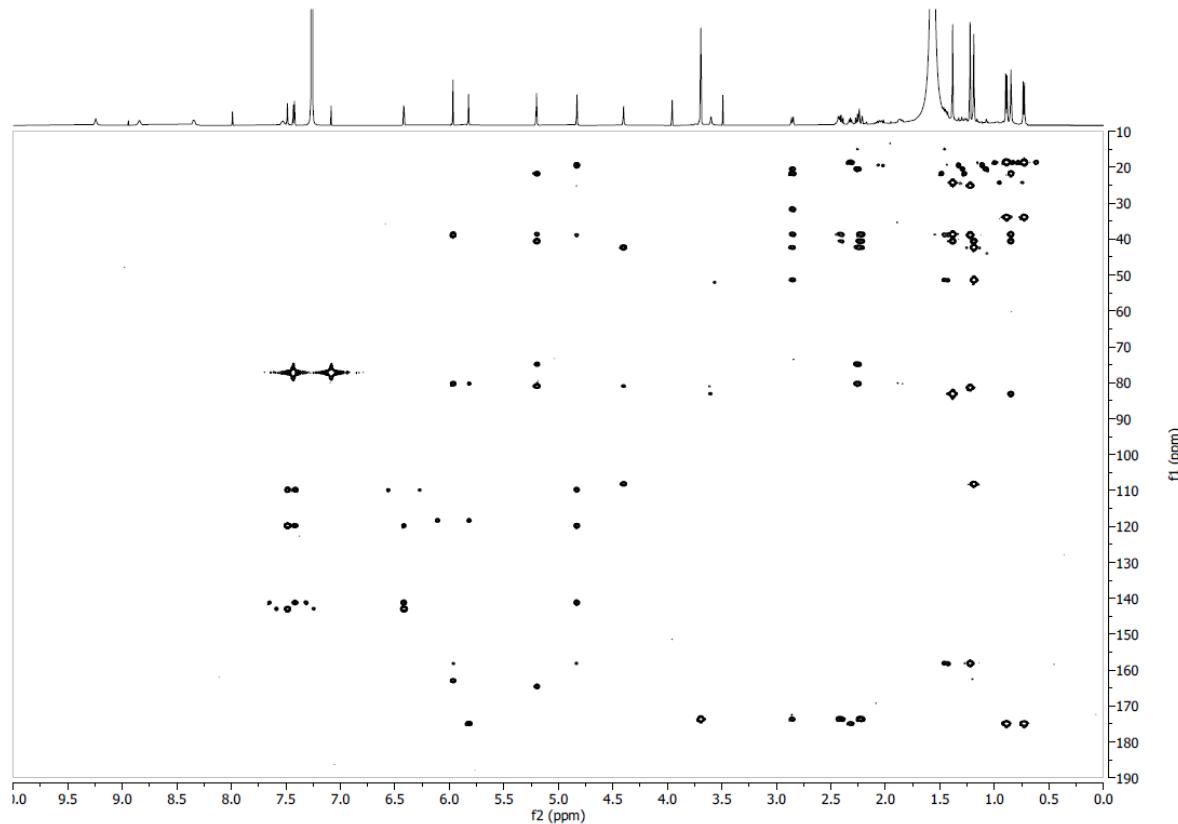
Supplementary Figure S4.2.139. ^1H NMR spectrum of compound **24** in CDCl_3 at 600 MHz



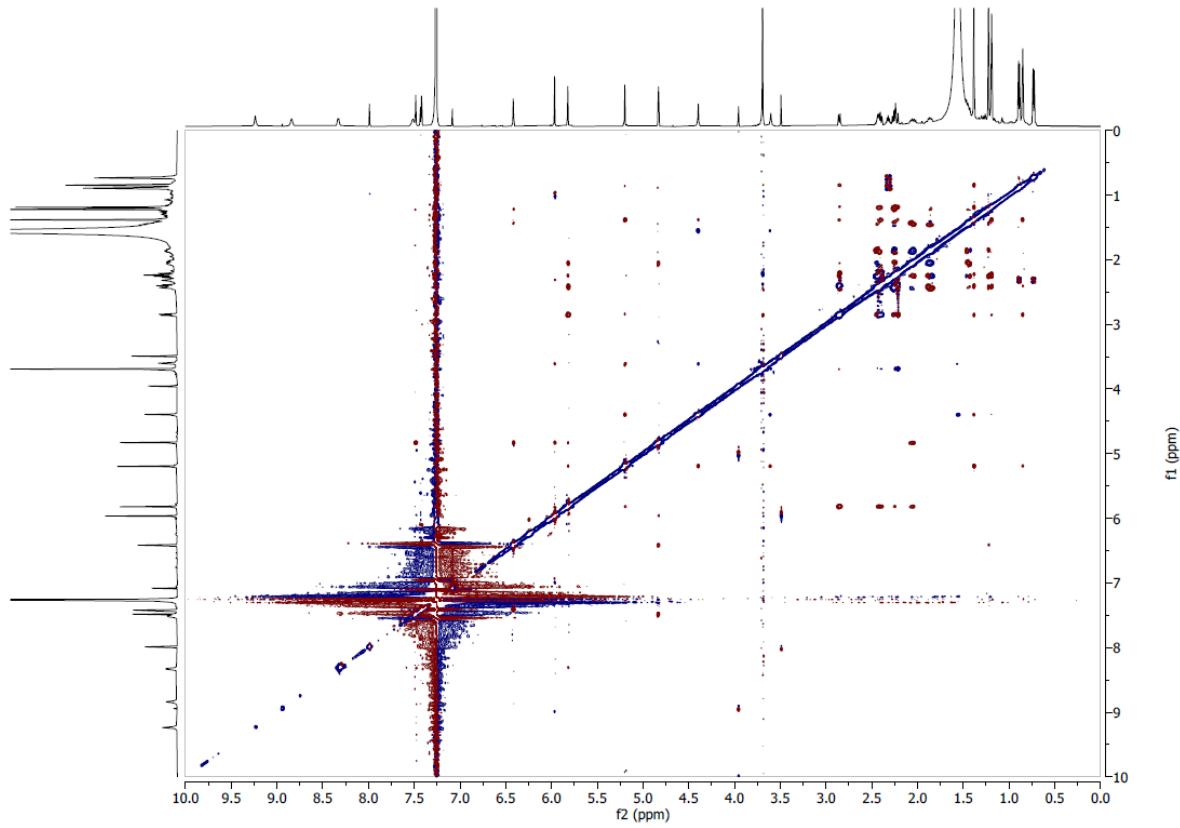
Supplementary Figure S4.2.140. COSY NMR spectrum of compound **24** in CDCl_3



Supplementary Figure S4.2.141. Edited HSQC NMR spectrum of compound **24** in CDCl_3

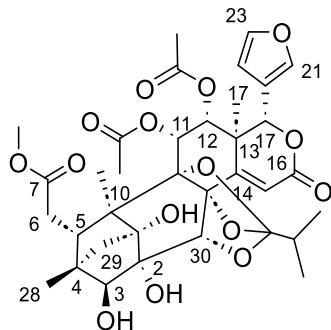


Supplementary Figure S4.2.142. HMBC NMR spectrum of compound **24** in CDCl_3

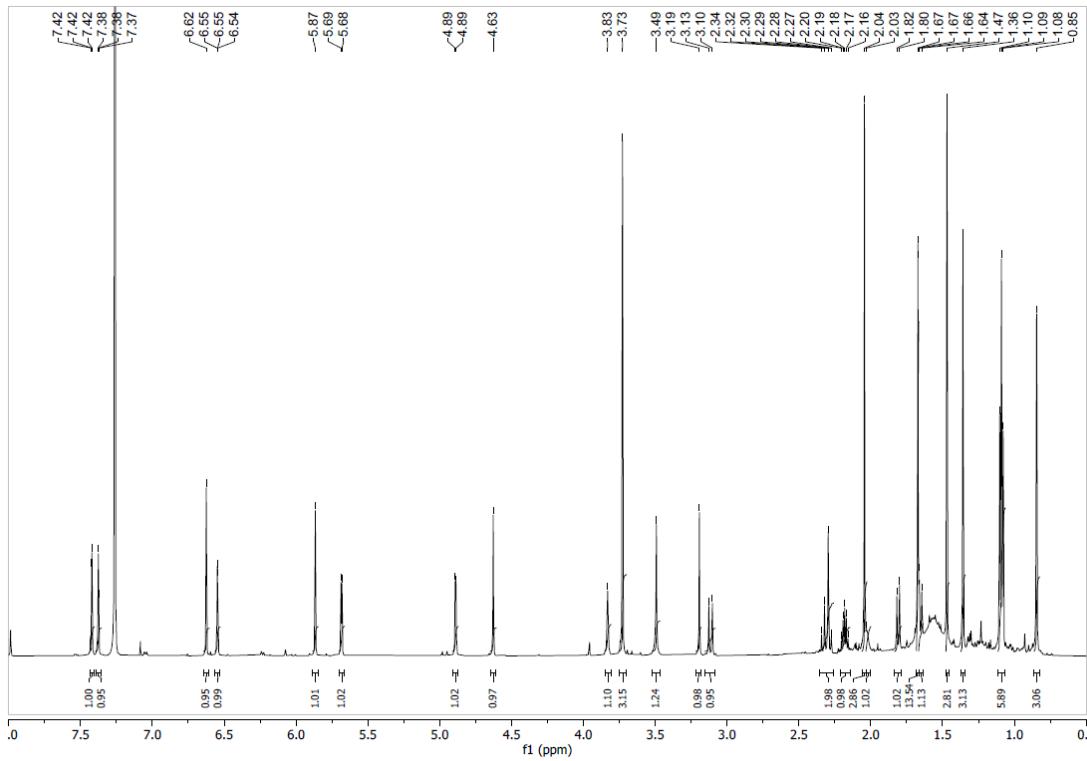


Supplementary Figure S4.2.143. ROESY NMR spectrum of compound **24** in CDCl_3

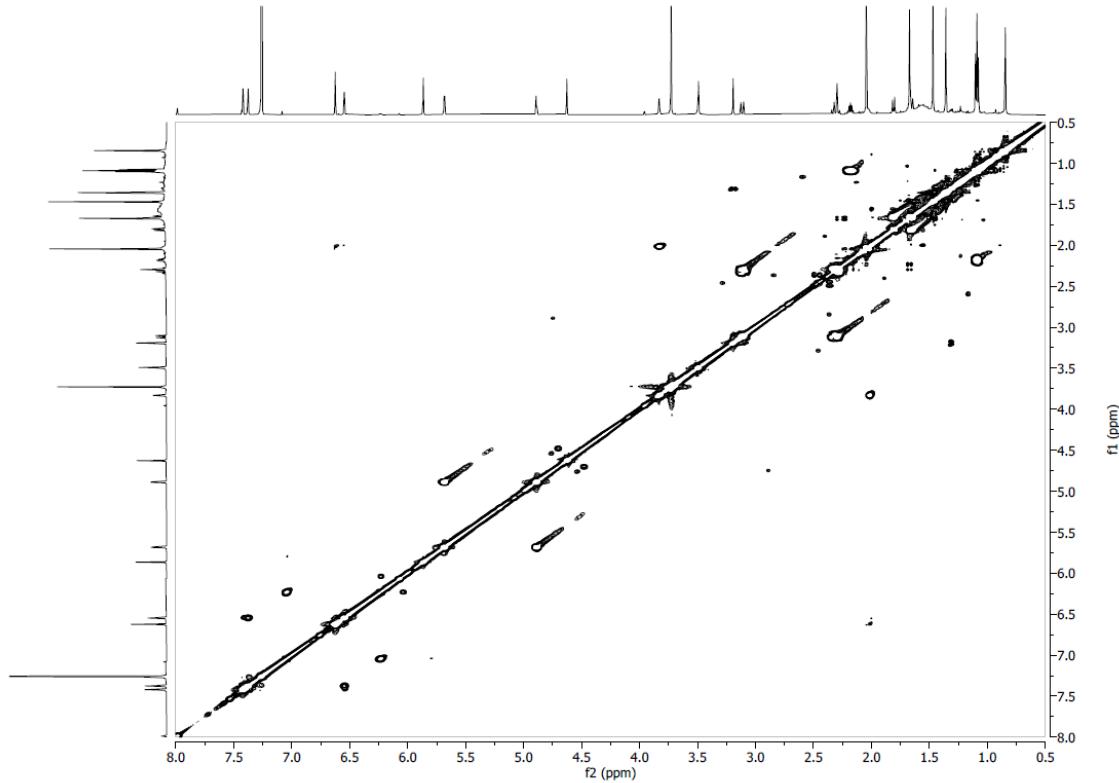
Compound **25**: Entanutilin I [81]. Amorphous white powder, HRESIMS m/z 703.2603 [$M+H$]⁺ (calculated for C₃₅H₄₃O₁₅, error 0.94 ppm); $[\alpha]_D^{20} +38$ (c 0.001 CHCl₃); UV (c 0.001, CHCl₃) λ_{max} 200nm.



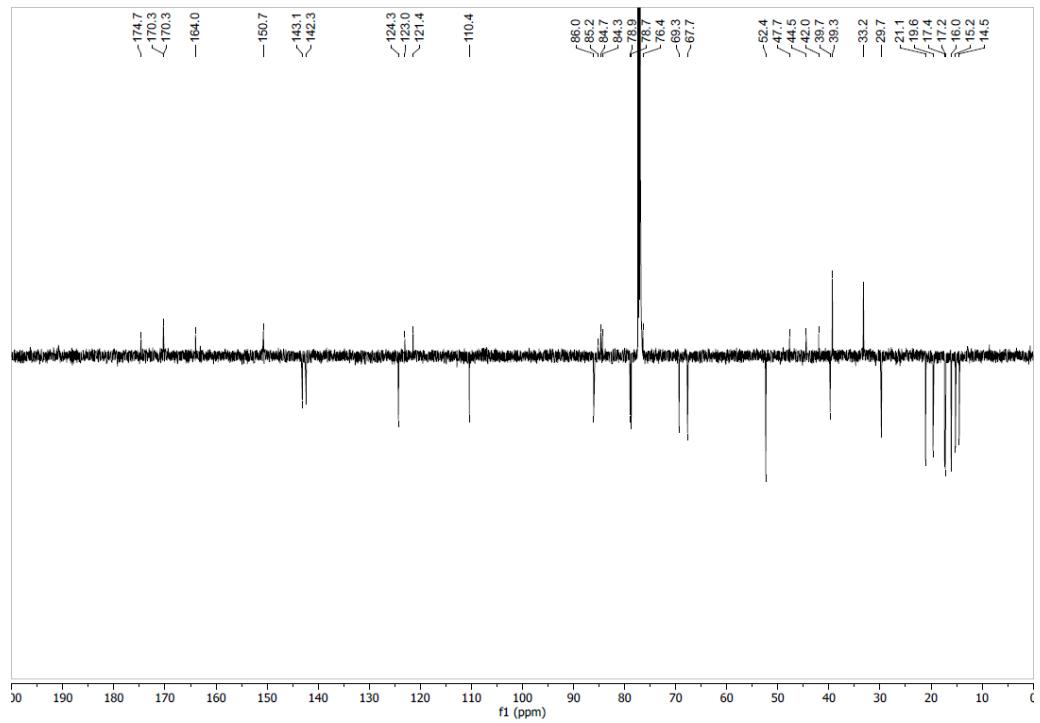
¹H NMR (CDCl₃, 600 MHz) δ 0.85 (3H, s, H₃-28), 1.08 (3H, d, J = 6.9 Hz, H₃-33), 1.10 (3H, d, J = 6.9 Hz, H₃-34), 1.36 (3H, s, H₃-19), 1.47 (3H, s, H₃-12b), 1.65 (1H, d, J = 11.3 Hz, H-29_{ProS}), 1.67 (3H, s, H₃-18), 1.81 (1H, d, J = 11.3 Hz, H-29_{ProR}), 2.03 (1H, s, OH-3), 2.04 (3H, s, H₃-11b), 2.18 (1H, hept, J = 6.9 Hz, H-32), 2.31 (2H, m, H-5, H-6''), 3.11 (1H, d, J = 14.7 Hz, H-6'), 3.19 (1H, s, OH-1), 3.49 (1H, s, OH-2), 3.73 (3H, s, OCH₃), 3.83 (1H, s, H-3), 4.63 (1H, s, H-30), 4.89 (1H, d, J = 3.9 Hz, H-12), 5.68 (1H, d, J = 3.8 Hz, H-11), 5.87 (1H, s, H-17), 6.55 (1H, t, J = 1.5 Hz, H-22), 6.62 (1H, s, H-15), 7.38 (1H, t, J = 1.5 Hz, H-23), 7.42 (1H, t, J = 1.5 Hz, H-21); ¹³C NMR (CDCl₃, 151 MHz) δ 14.5 (CH₃-28), 15.2 (CH₃-18), 16.0 (CH₃-19), 17.2 (CH₃-34), 17.4 (CH₃-33), 19.6 (CH₃-11b), 21.1 (CH₃-12b), 29.7 (CH-32), 33.2 (CH₂-6), 39.3 (CH₂-29), 39.7 (CH-5), 42.0 (C-13), 44.5 (C-4), 47.7 (C-10), 52.4 (OCH₃), 67.7 (CH-11), 69.3 (CH-12), 76.4 (C-2), 78.7 (CH-30), 78.9 (CH-17), 84.3 (C-8), 84.7 (C-1), 85.2 (C-9), 86.0 (CH-3), 110.4 (CH-22), 121.4 (C-20), 123.0 (C-31), 124.3 (CH-15), 142.3 (CH-21), 143.1 (CH-23), 150.7 (C-14), 164.0 (C-16), 170.3 (12a), 170.3 (11a), 174.7 (C-7). Supplementary Figures S4.2.144-S4.2.149.



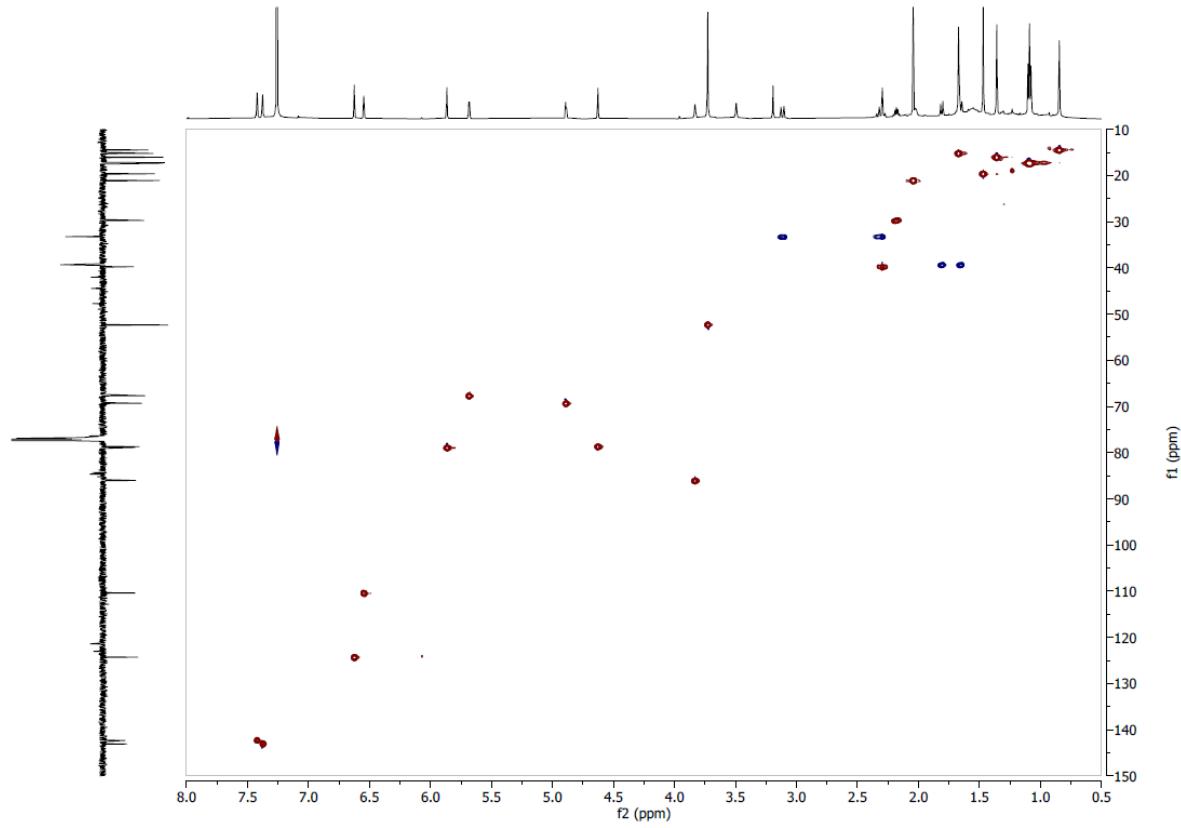
Supplementary Figure S4.2.144. ^1H NMR spectrum of compound **25** in CDCl_3 at 600 MHz



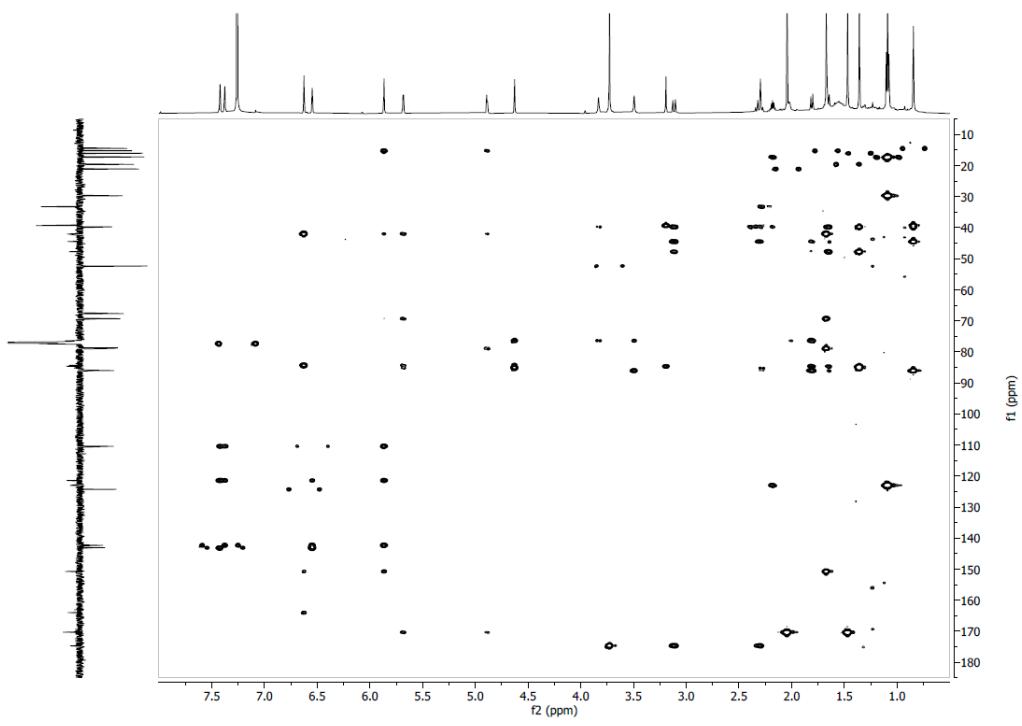
Supplementary Figure S4.2.145. COSY NMR spectrum of compound **25** in CDCl_3



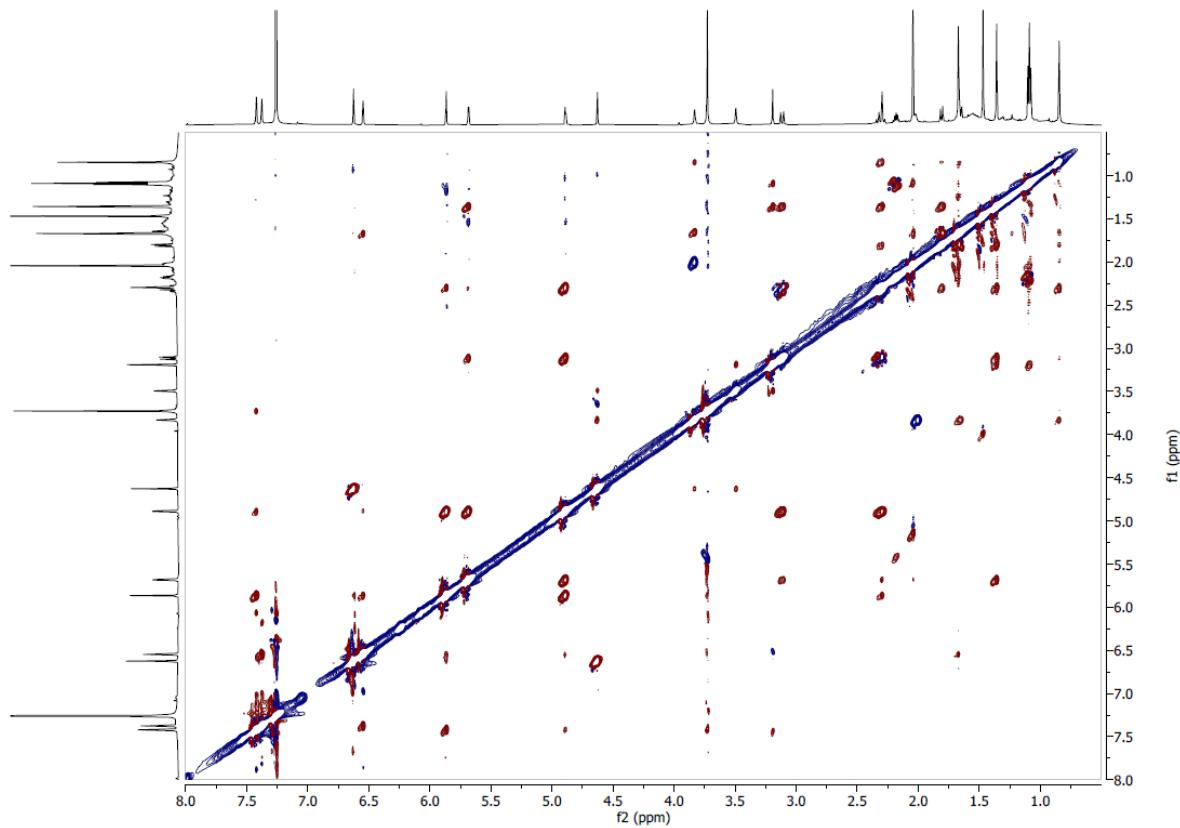
Supplementary Figure S4.2.146. ^{13}C -DEPTQ NMR spectrum of compound **25** in CDCl_3 at 151 MHz



Supplementary Figure S4.2.147. Edited HSQC NMR spectrum of compound **25** in CDCl_3

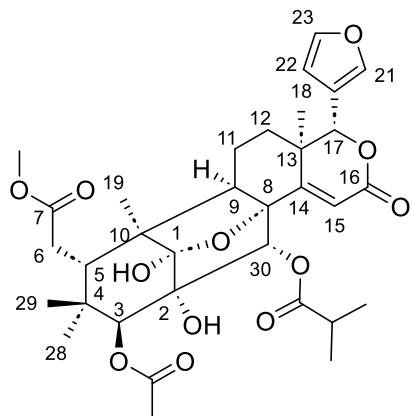


Supplementary Figure S4.2.148. HMBC NMR spectrum of compound **25** in CDCl_3

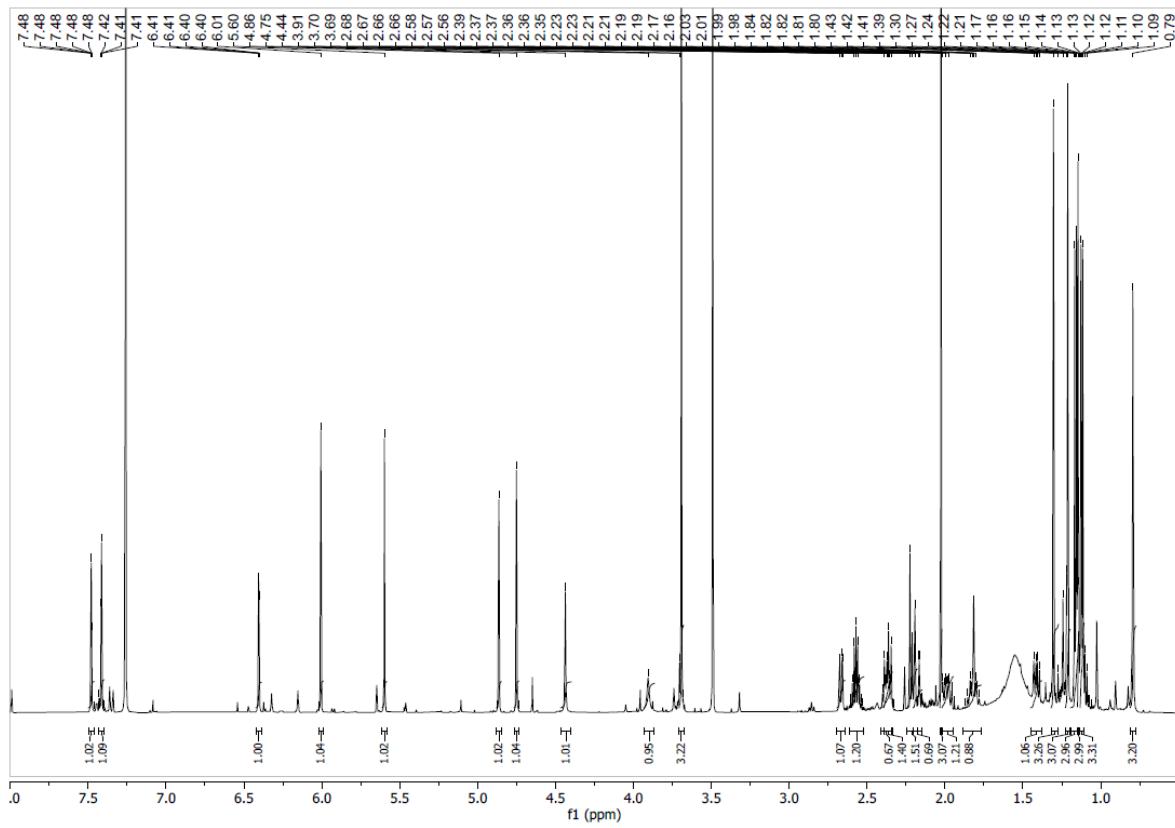


Supplementary Figure S4.2.149. ROESY NMR spectrum of compound **25** in CDCl_3

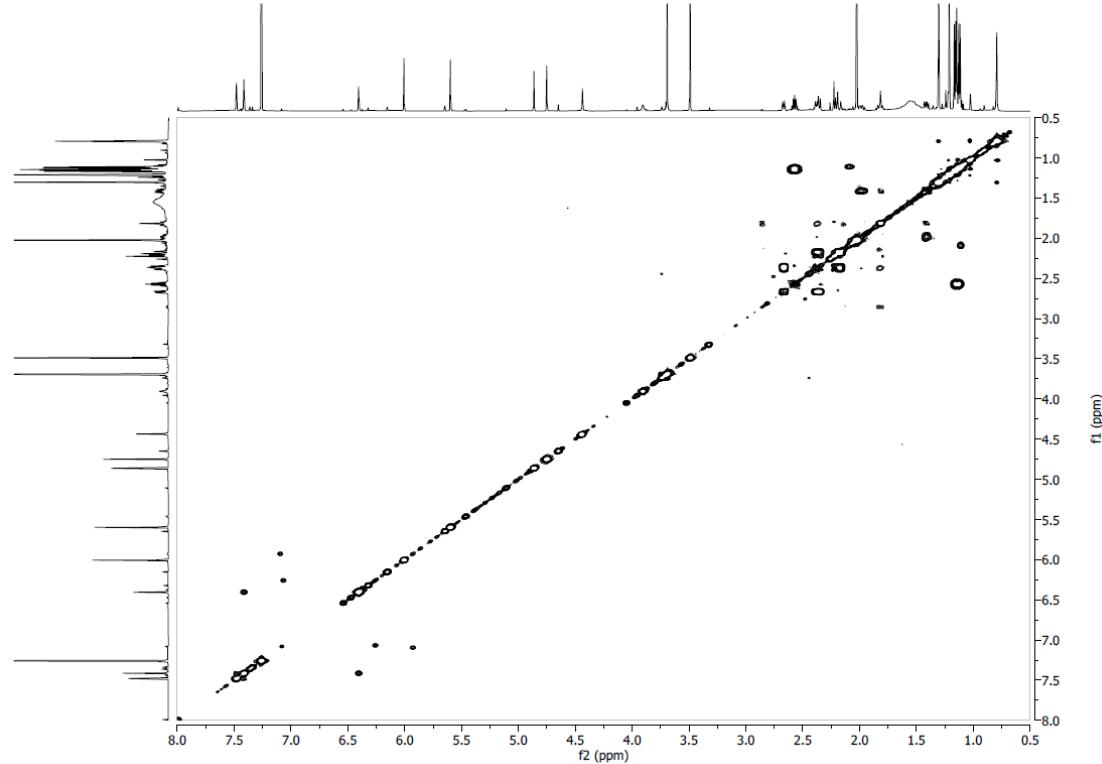
Compound 26: Utilin C [85]. Amorphous white powder, HRESIMS m/z 631.2758 [$M+H$]⁺ (calculated for $C_{33}H_{42}O_{12}$, error 1.45 ppm); $[\alpha]_D^{20} +2$ (c 0.002 CHCl₃); UV (c 0.002, CHCl₃) λ_{max} 198, 225 nm.



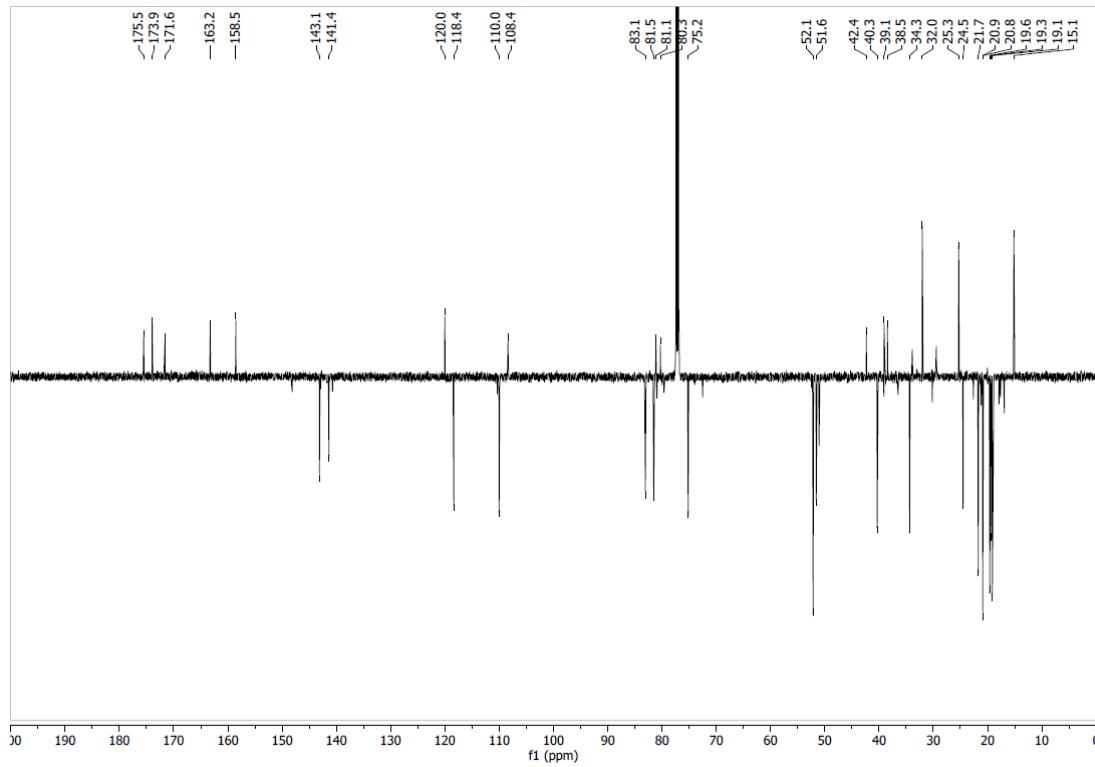
¹H NMR (CDCl₃, 600 MHz) δ 0.79 (3H, s, H₃-29), 1.12 (3H, d, J = 7.0 Hz, H₃-30d), 1.15 (3H, s, H₃-19), 1.16 (3H, d, J = 7.0 Hz, H₃-30c), 1.21 (3H, s, H₃-18), 1.30 (3H, s, H₃-28), 1.42 (1H, dd, J = 13.8, 8.5 Hz, H-12 α), 1.82 (1H, tt, J = 13.8, 11.4, 10.3, 8.5 Hz, H-11 α), 1.99 (1H, td, J = 13.8, 11.4, 8.8 Hz, H-12 β), 2.03 (3H, s, H₃-3b), 2.18 (1H, dd, J = 16.4, 2.1 Hz, H-6¹¹), 2.21 (2H, t, J = 10.3, 9.4 Hz, H-9), 2.37 (1H, dd, J = 16.4, 10.2 Hz, H-6¹), 2.37 (1H, dt, J = 13.8, 9.4, 8.8 Hz, H-11 β), 2.57 (1H, hept, J = 7.0 Hz, H-30b), 2.67 (1H, dd, J = 10.2, 2.1 Hz, H-5), 3.69 (3H, s, OCH₃), 3.91 (1H, s, OH-2), 4.44 (1H, s, OH-1), 4.75 (1H, s, H-3), 4.86 (1H, s, H-17), 5.60 (1H, s, H-30), 6.01 (1H, s, H-15), 6.41 (1H, t, J = 1.7, 0.8 Hz, H-22), 7.41 (1H, t, J = 1.7 Hz, H-23), 7.48 (1H, t, J = 1.7, 0.8 Hz, H-21); ¹³C NMR (CDCl₃, 151 MHz) δ 15.1 (CH₂-11), 19.1 (CH₃-30d), 19.3 (CH₃-30c), 19.6 (CH₃-18), 20.8 (CH₃-19), 20.9 (CH₃-3b), 21.7 (CH₃-28), 24.5 (CH₃-29), 25.3 (CH₂-12), 32.0 (CH₂-6), 34.3 (CH-30b), 38.5 (C-4), 39.1 (C-13), 40.3 (CH-5), 42.4 (C-10), 51.6 (CH-9), 52.1 (OCH₃), 75.2 (CH-30), 80.3 (C-8), 81.1 (C-2), 81.5 (CH-17), 83.1 (CH-3), 108.4 (C-1), 110.0 (CH-22), 118.4 (CH-15), 120.0 (C-20), 141.4 (CH-21), 143.1 (CH-23), 158.5 (C-14), 163.2 (C-16), 171.6 (C-3a), 173.9 (C-7), 175.5 (C-30a). **Supplementary Figures S4.2.150–S4.2.155.**



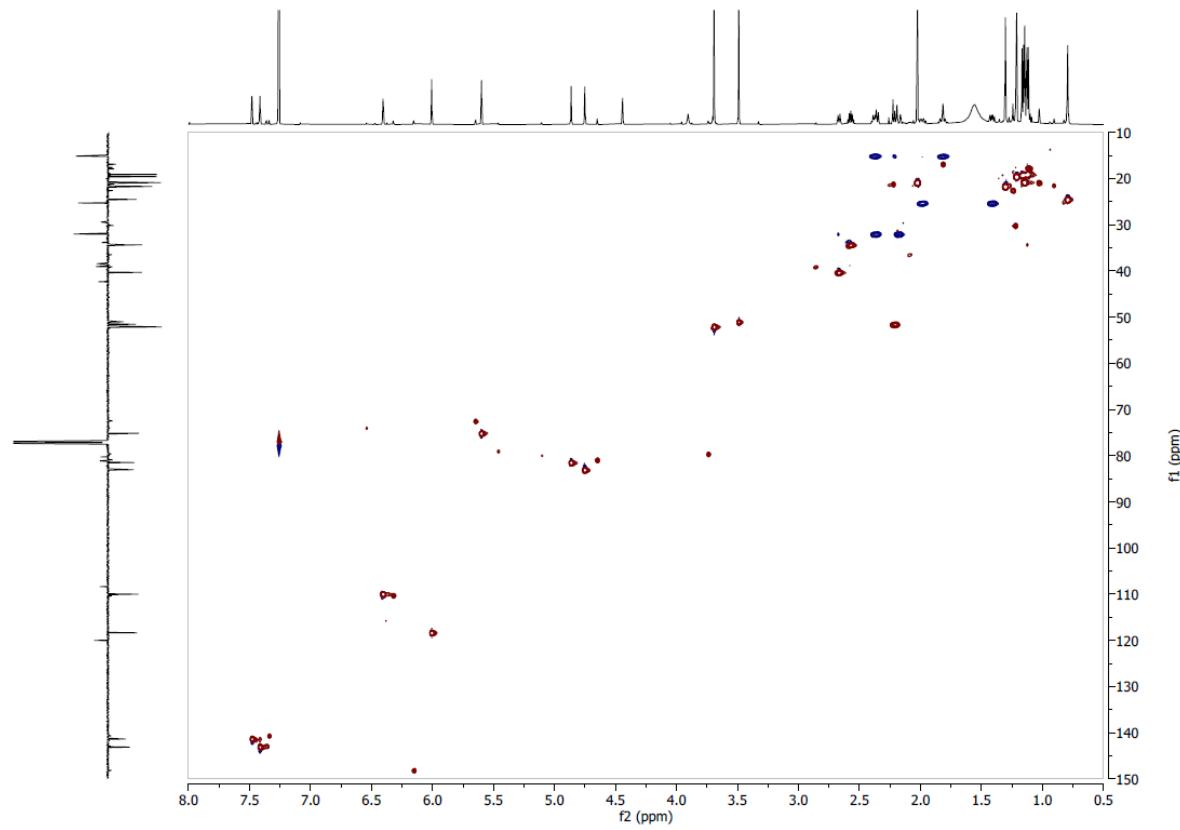
Supplementary Figure S4.2.150. ^1H NMR spectrum of compound **26** in CDCl_3 at 600 MHz



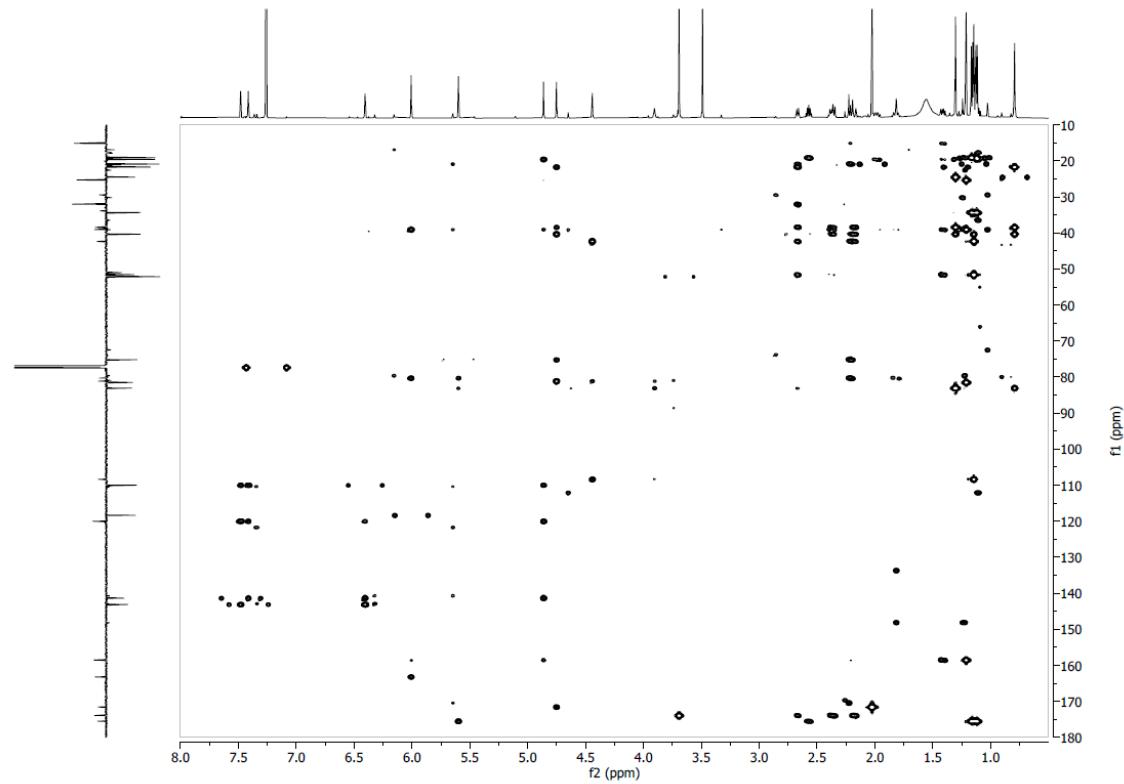
Supplementary Figure S4.2.151. COSY NMR spectrum of compound **26** in CDCl_3



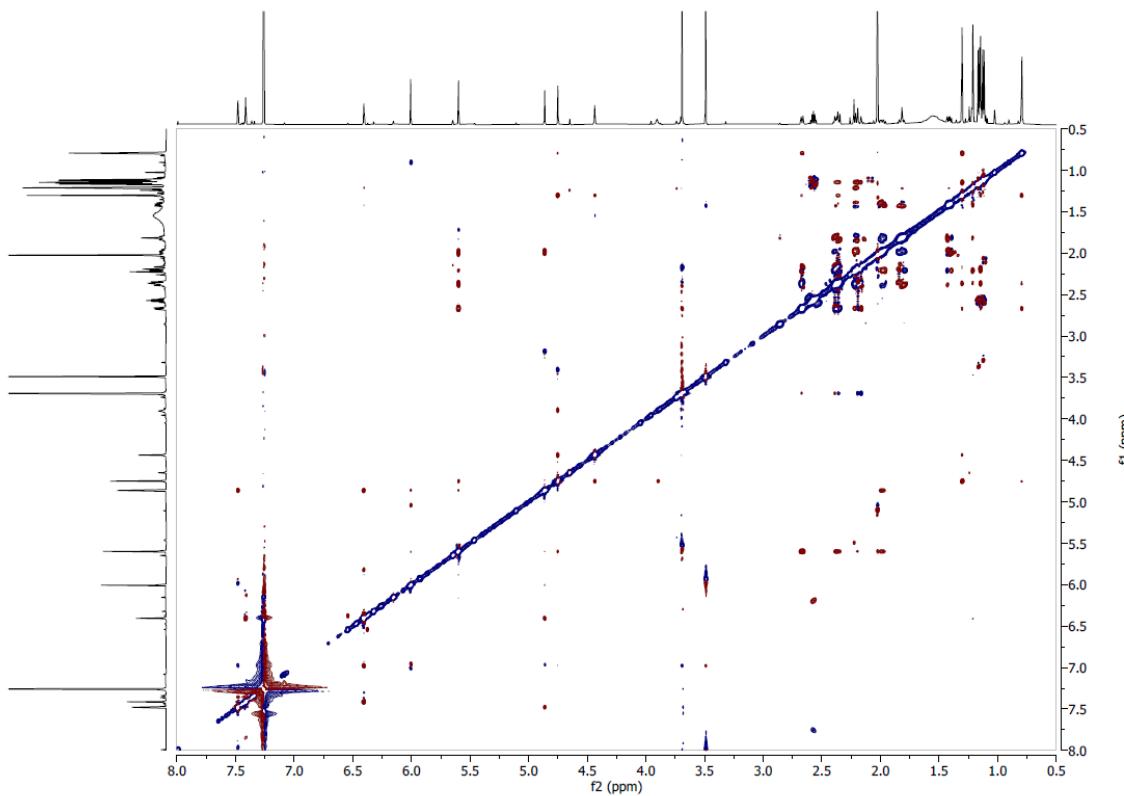
Supplementary Figure S4.2.152. ^{13}C -DEPTQ NMR spectrum of compound **26** in CDCl_3 at 151 MHz



Supplementary Figure S4.2.153. Edited HSQC NMR spectrum of compound **26** in CDCl_3

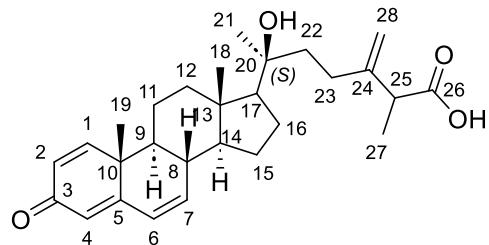


Supplementary Figure S4.2.154. HMBC NMR spectrum of compound **26** in CDCl_3



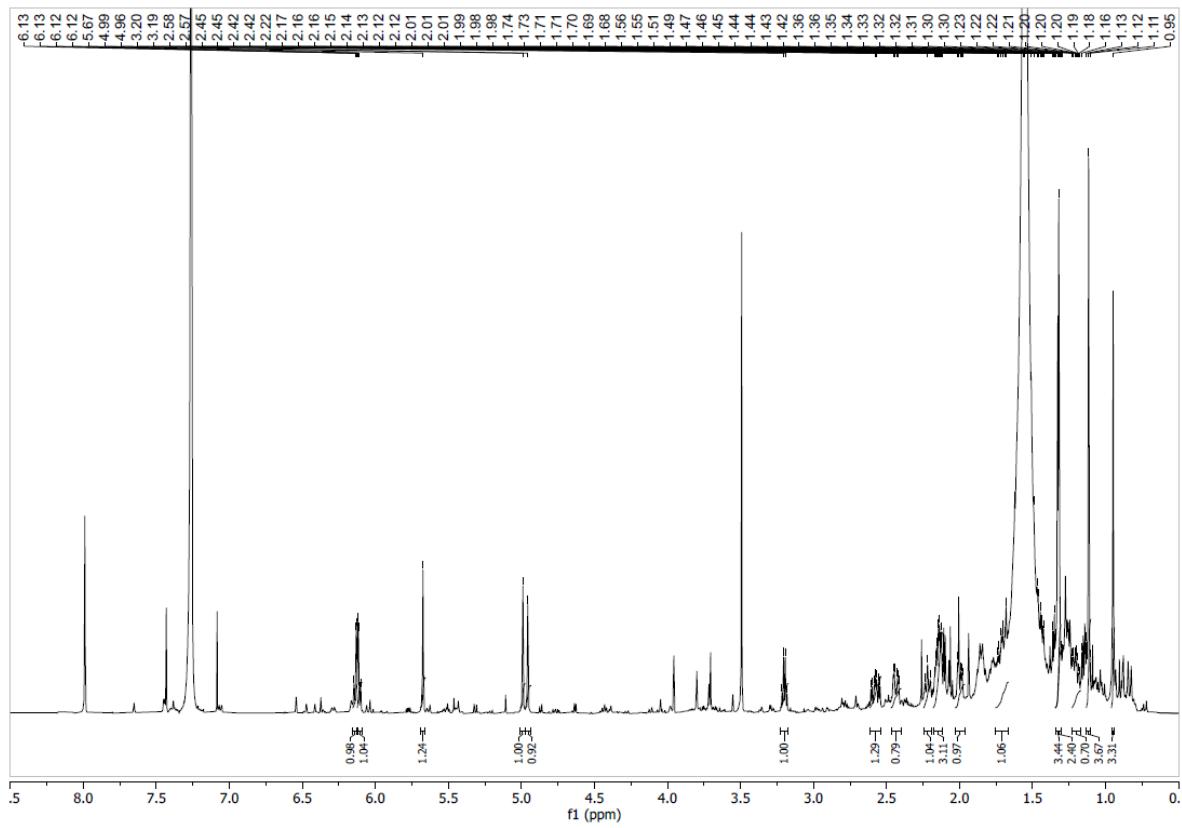
Supplementary Figure S4.2.155. ROESY NMR spectrum of compound **26** in CDCl_3

Compound **27**: 20-hydroxy-3-oxo-ergosta-1,4,6,24-tetraen-26-oic acid. Amorphous white powder, HRESIMS m/z 441.2995 [M+H]⁺ (calculated for C₂₈H₄₁O₄, error -2.91 ppm); $[\alpha]_D^{20}$ -10 (c 0.0003 CHCl₃); UV (c 0.0003, CHCl₃) λ_{max} 200, 227, 288 nm.

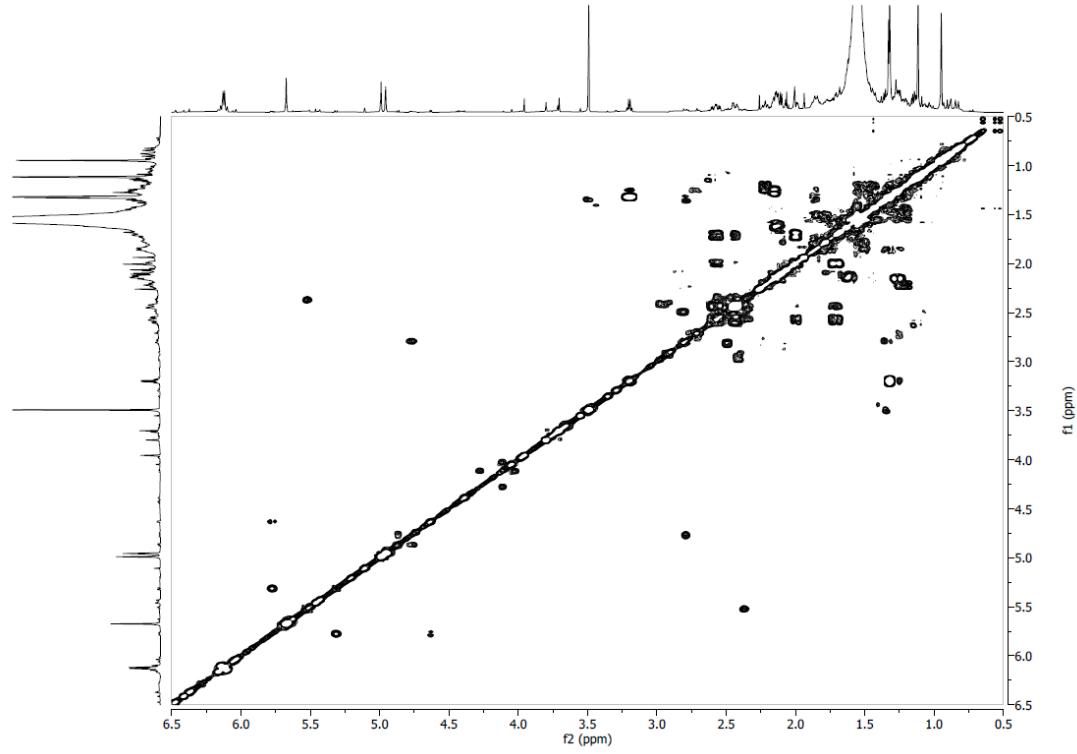


¹H NMR (CDCl₃, 600 MHz) δ 0.95 (3H, s, H₃-18), 1.12 (3H, s, H₃-19), 1.20 (1H, m, H-9), 1.24 (1H, m, H-14), 1.27 (1H, m, H-12a), 1.32 (3H, s, H₃-21), 1.32 (2H, d, J = 7.1 Hz, H₃-27), 1.34 (1H, m, H-15¹¹), 1.44 (1H, m, H-11b), 1.50 (1H, m, H-17), 1.55 (1H, m, H-11a), 1.61 (2H, m, H₂-22), 1.71 (1H, td, J = 14.0, 5.0 Hz, H-1 α), 1.77 (1H, m, H-16¹¹), 1.85 (2H, m, H-15¹, H-16¹), 2.00 (1H, ddd, J = 14.0, 5.5, 1.6 Hz, H-1 β), 2.14 (2H, m, H₂-23), 2.16 (1H, m, H-12b), 2.22 (1H, t, J = 10.7 Hz, H-8), 2.43 (1H, dt, J = 19.3, 5.0, 1.6 Hz, H-2 α), 2.58 (1H, ddd, J = 19.3, 14.5, 5.5 Hz, H-2 β), 3.20 (1H, q, J = 7.1 Hz, H-25), 4.96 (1H, s, H-28¹¹), 4.99 (1H, s, H-28¹), 5.67 (1H, s, H-4), 6.11 (1H, dd, J = 9.8, 2.2 Hz, H-6), 6.14 (1H, d, J = 9.8 Hz, H-7); ¹³C NMR (CDCl₃, 151 MHz) δ 13.7 (CH₃-18), 16.4 (CH₃-19), 16.6 (CH₃-27), 20.7 (CH₂-11), 22.6 (CH₂-16), 23.4 (CH₂-15), 26.1 (CH₃-21), 29.4 (CH₂-23), 34.0 (CH₂-1), 34.1 (CH₂-2), 36.2 (C-10), 37.2 (CH-8), 40.1 (CH₂-12), 41.5 (CH₂-22), 44.0 (C-13), 45.0 (CH-25), 50.8 (CH-9), 53.7 (CH-14), 58.4 (CH-17), 75.3 (C-20), 111.9 (CH₂-28), 123.8 (CH-4), 128.2 (CH-6), 141.3 (CH-7), 148.2 (C-24), 164.0 (C-5), 175.5 (C-26), 199.7 (C-3).

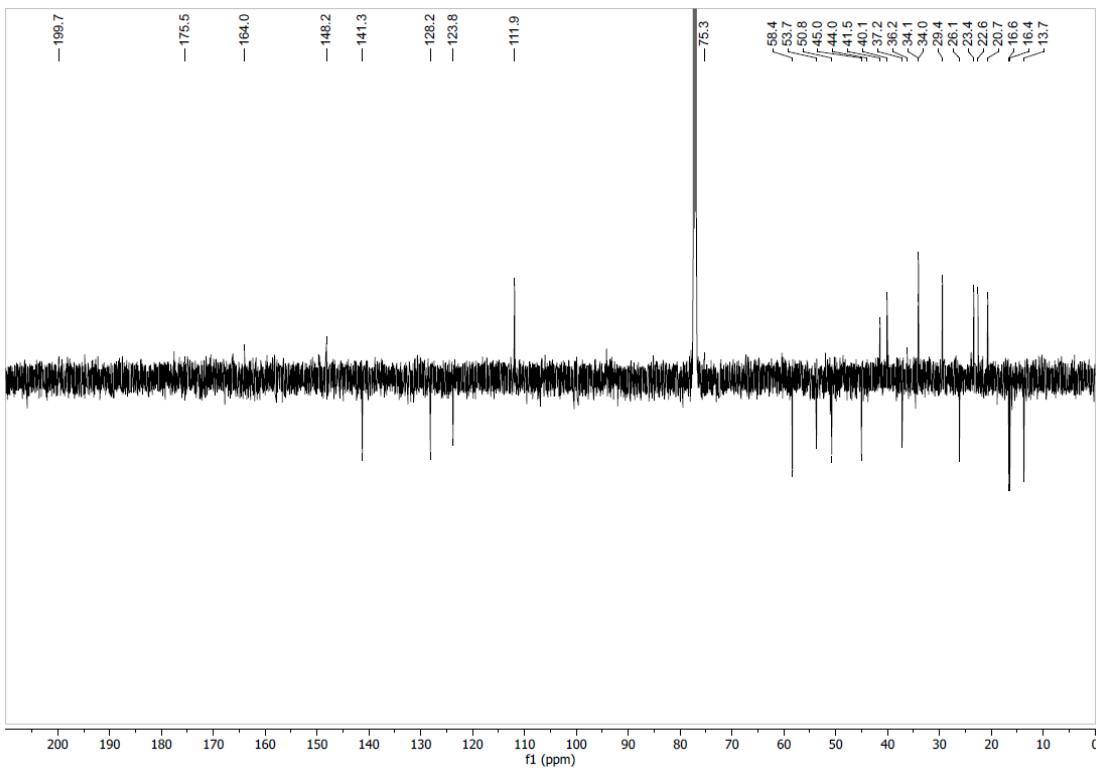
Supplementary Figures S4.2.156-S4.2.161.



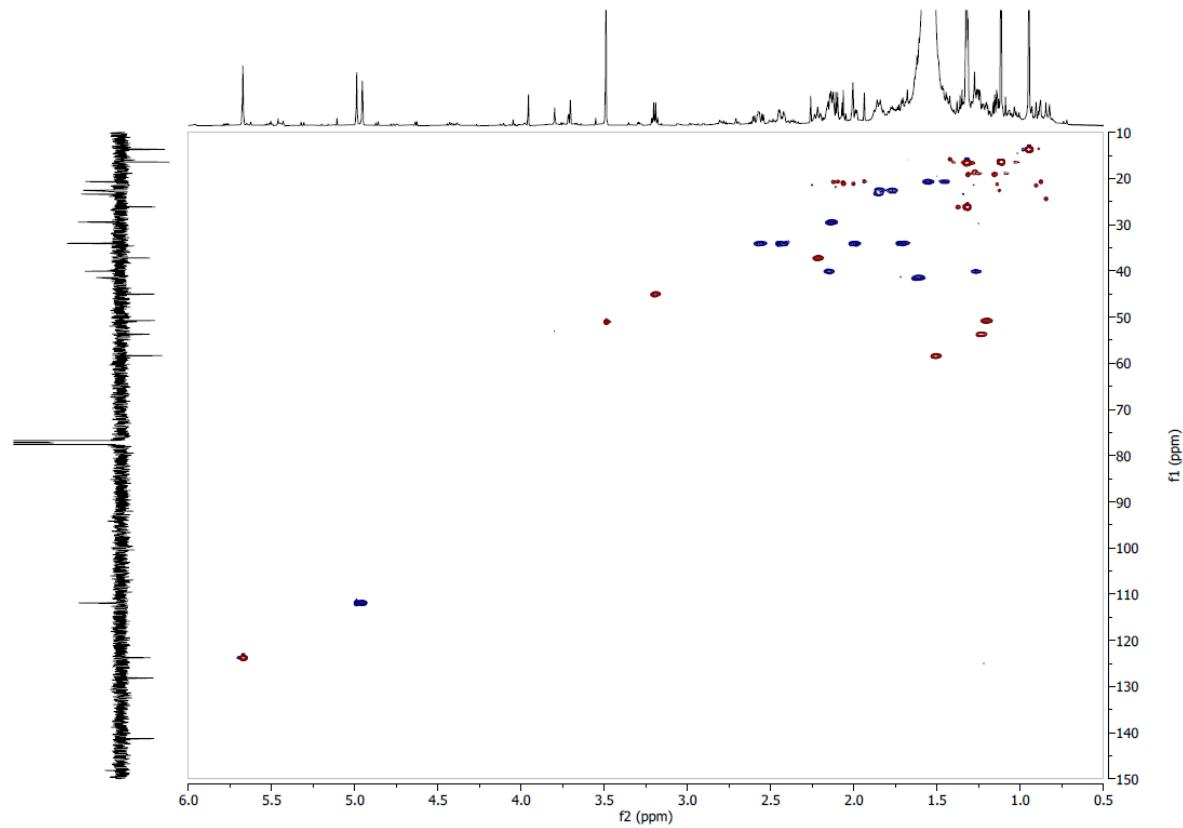
Supplementary Figure S4.2.156. ^1H NMR spectrum of compound **27** in CDCl_3 at 600 MHz



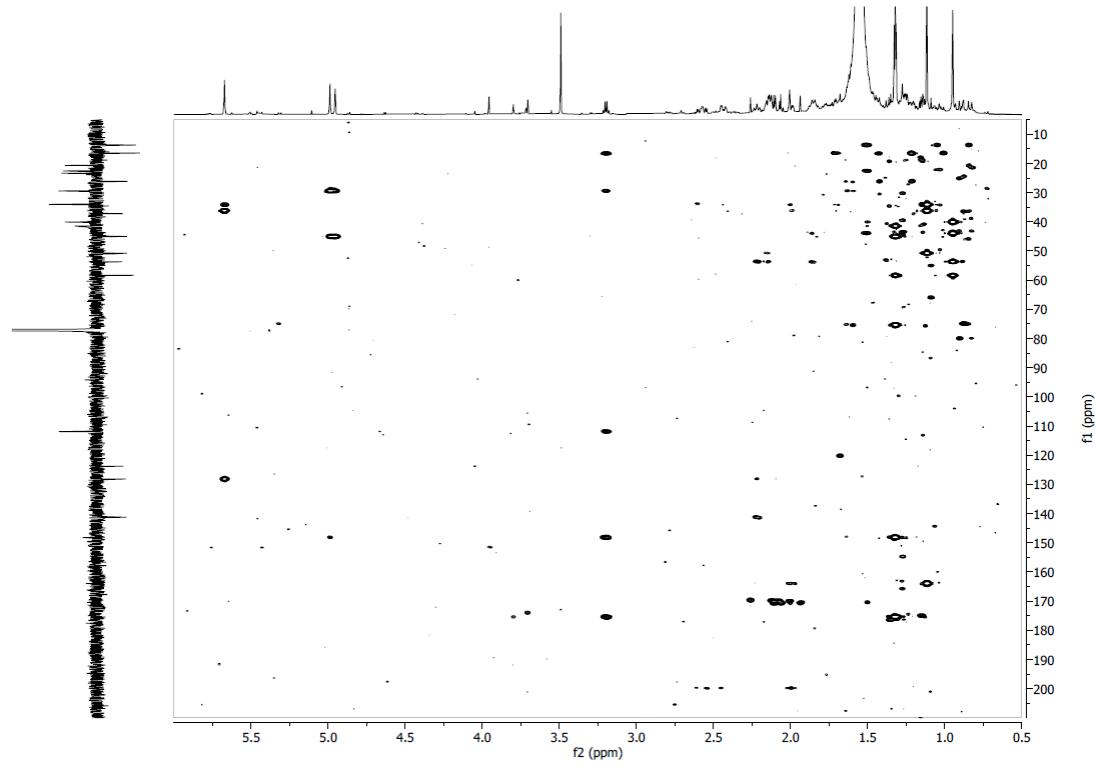
Supplementary Figure S4.2.157. COSY NMR spectrum of compound **27** in CDCl_3



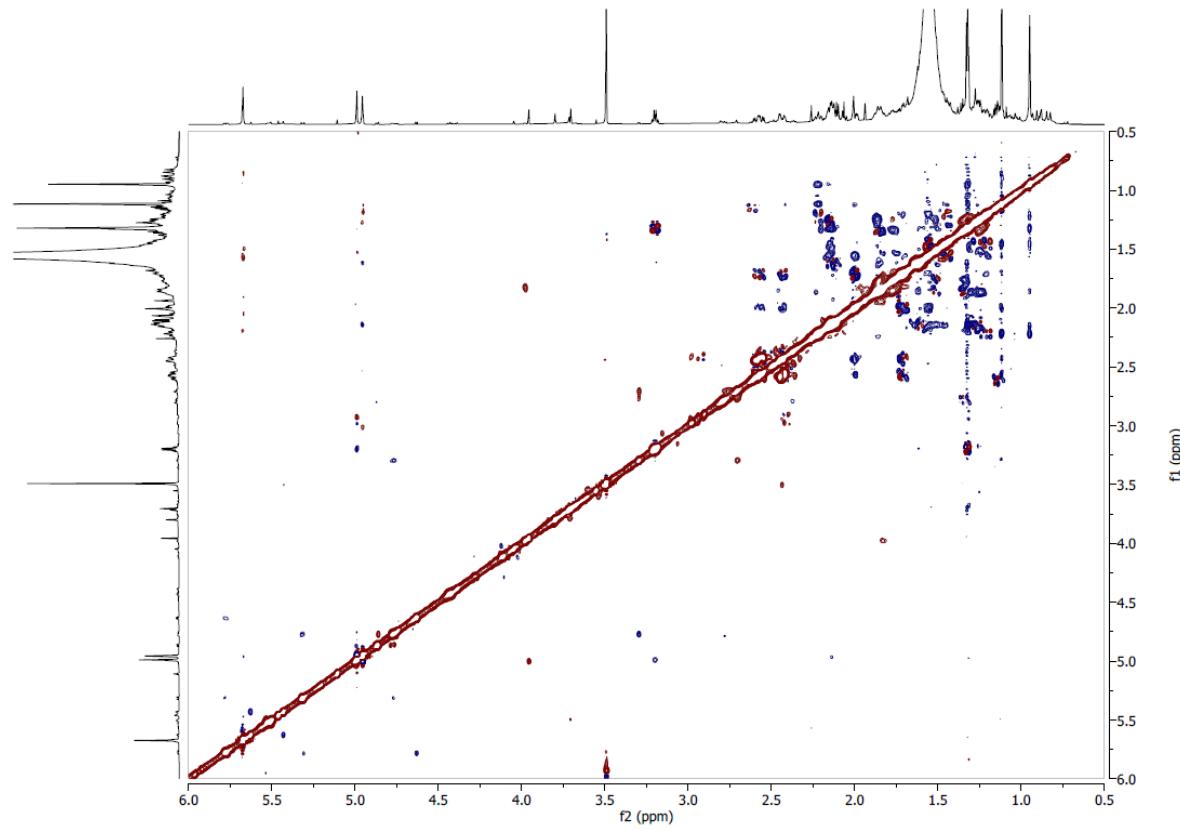
Supplementary Figure S4.2.158. ^{13}C -DEPTQ NMR spectrum of compound **27** in CDCl_3 at 151 MHz



Supplementary Figure S4.2.159. Edited HSQC NMR spectrum of compound **27** in CDCl_3

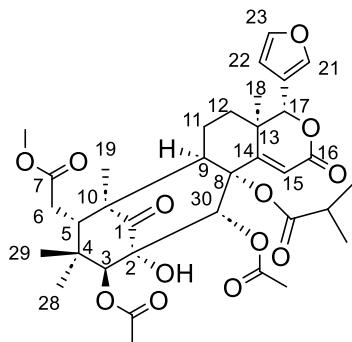


Supplementary Figure S4.2.160. HMBC NMR spectrum of compound **27** in CDCl_3

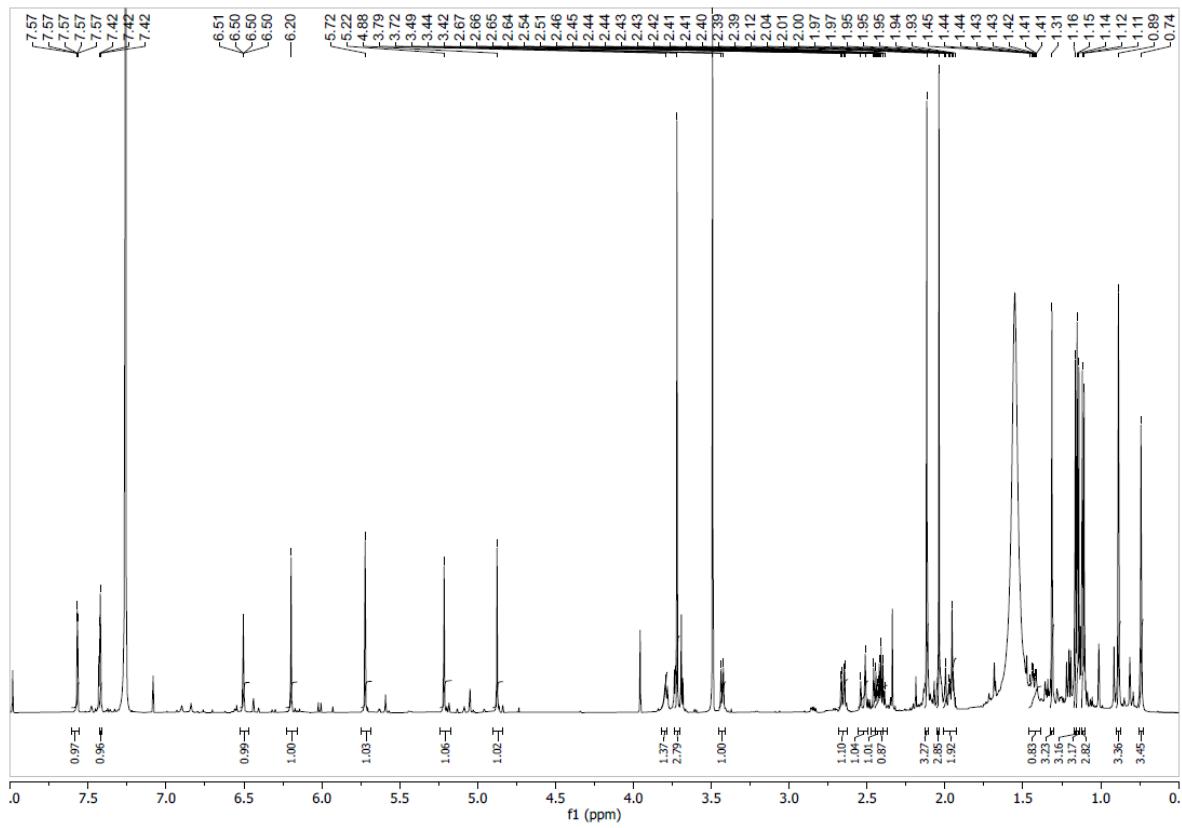


Supplementary Figure S4.2.161. ROESY NMR spectrum of compound **27** in CDCl_3

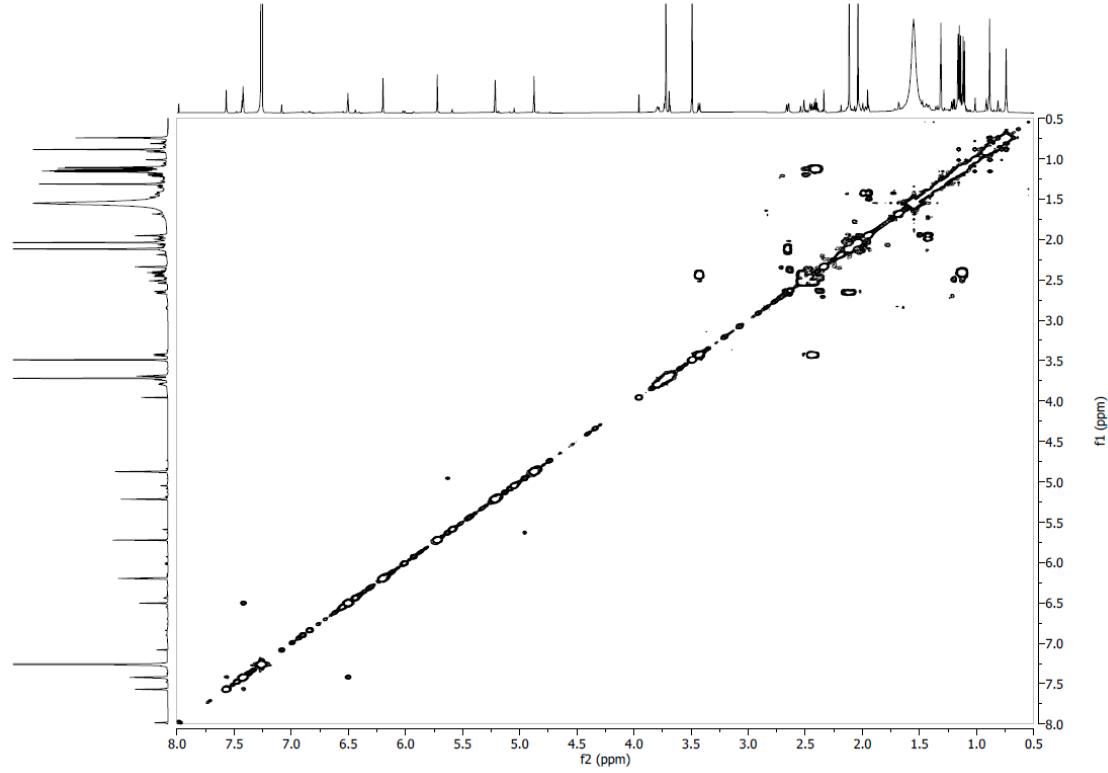
Compound 28: Utilin B [83]. Amorphous white powder, HRESIMS m/z 673.2856[M+H]⁺ (calculated for C₃₅H₄₄O₁₃, error 0.25 ppm); $[\alpha]_D^{20} -7$ (c 0.0007 CHCl₃); UV (c 0.0007, CHCl₃) λ_{max} 198, 217 nm.



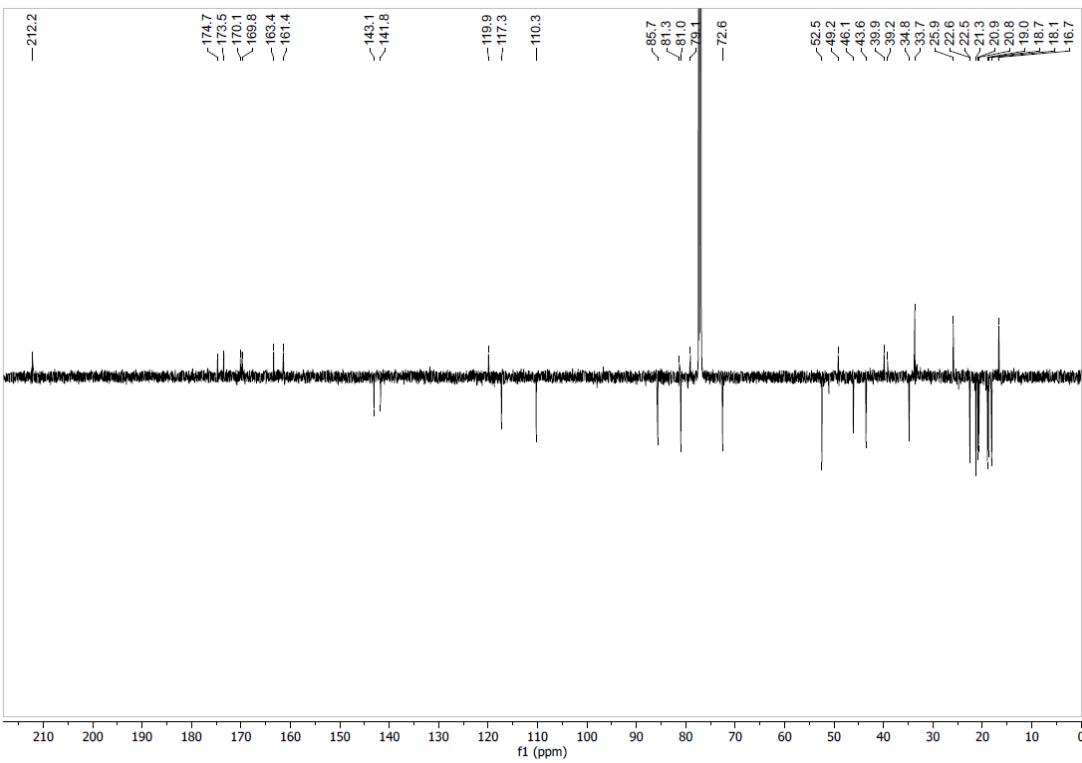
¹H NMR (CDCl₃, 600 MHz) δ 0.74 (3H, s, H₃-29), 0.89 (3H, s, H₃-28), 1.11 (3H, d, J = 7.0 Hz, H₃-8d), 1.15 (3H, d, J = 7.0 Hz, H₃-8c), 1.16 (3H, s, H₃-19), 1.31 (3H, s, H₃-18), 1.43 (1H, m, H-12a), 1.97 (1H, m, H-12b), 2.02 (1H, m, H-11a), 2.04 (3H, s, H₃-3b), 2.12 (3H, s, H₃-30b), 2.13 (1H, m, H-11b), 2.41 (1H, hept, J = 7.0 Hz, H-8b), 2.44 (1H, dd, J = 17.6, 8.9 Hz, H-6''), 2.53 (1H, d, J = 17.6 Hz, H-6''), 2.66 (1H, dd, J = 11.6, 2.7 Hz, H-9), 3.43 (1H, d, J = 8.9 Hz, H-5), 3.72 (3H, s, OCH₃), 3.79 (1H, s, OH-2), 4.88 (1H, s, H-3), 5.22 (1H, s, H-17), 5.72 (1H, s, H-15), 6.20 (1H, s, H-30), 6.50 (1H, t, J = 1.8, 0.9 Hz, H-22), 7.42 (1H, t, J = 1.7 Hz, H-23), 7.57 (1H, t, J = 1.7, 0.9 Hz, H-21); ¹³C NMR (CDCl₃, 151 MHz) δ 16.7 (CH₂-11), 18.1 (CH₃-8d), 18.7 (CH₃-8c), 19.0 (CH₃-18), 20.8 (CH₃-3b), 20.9 (CH₃-19), 21.3 (CH₃-30b), 22.5 (CH₃-28), 22.6 (CH₃-29), 25.9 (CH₂-12), 33.7 (CH₂-6), 34.8 (CH-8b), 39.2 (C-13), 39.9 (C-4), 43.6 (CH-5), 46.1 (CH-9), 49.2 (C-10), 52.5 (OCH₃), 72.6 (CH-30), 79.1 (C-2), 81.0 (CH-17), 81.3 (C-8), 85.7 (CH-3), 110.3 (CH-22), 117.3 (CH-15), 119.9 (C-20), 141.8 (CH-21), 143.1 (CH-23), 161.4 (C-14), 163.4 (C-16), 169.8 (C-30a), 170.1 (C-3a), 173.5 (C-7), 174.7 (C-8a), 212.2 (C-1). **Supplementary Figures S4.2.162–S4.2.167.**



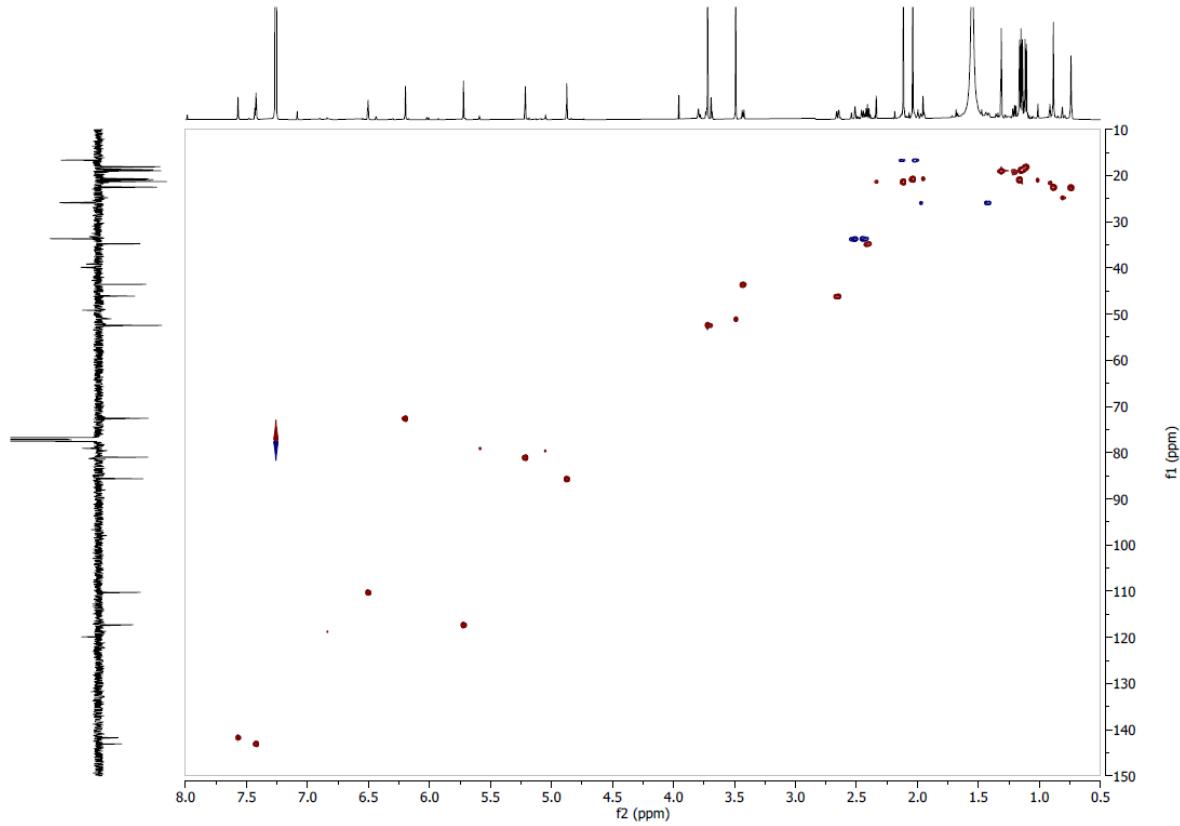
Supplementary Figure S4.2.162. ^1H NMR spectrum of compound **28** in CDCl_3 at 600 MHz



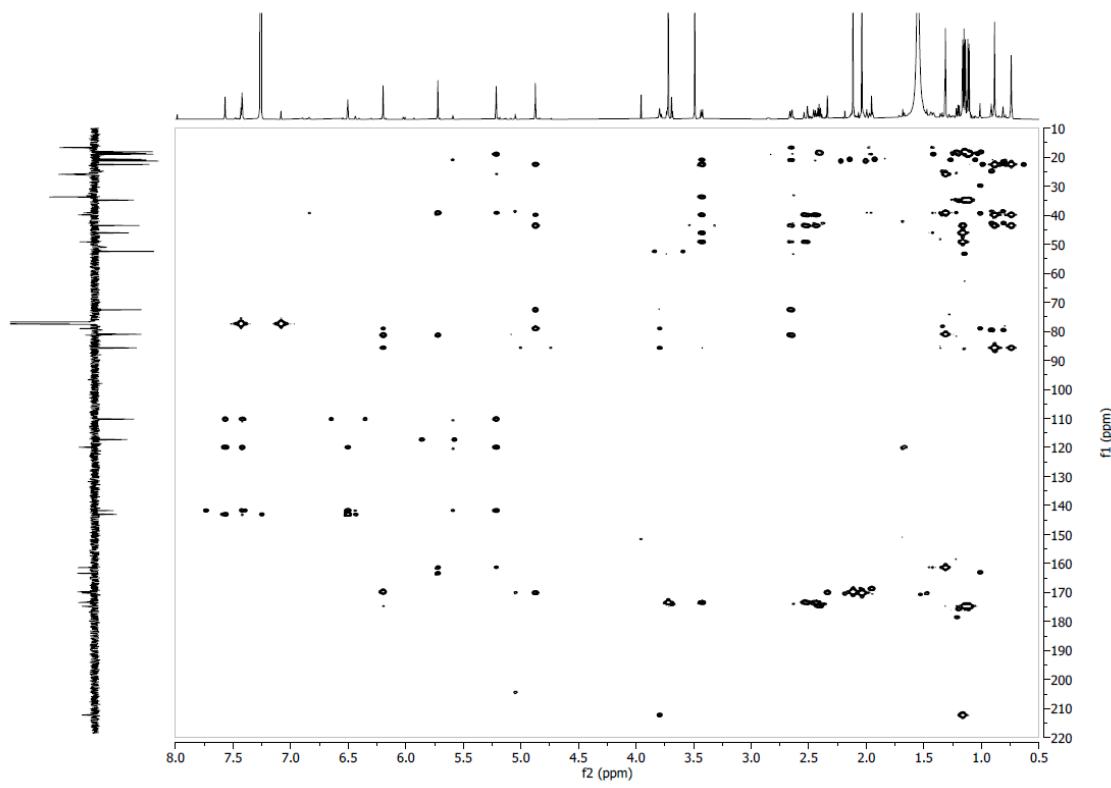
Supplementary Figure S4.2.163. COSY NMR spectrum of compound 28 in CDCl_3



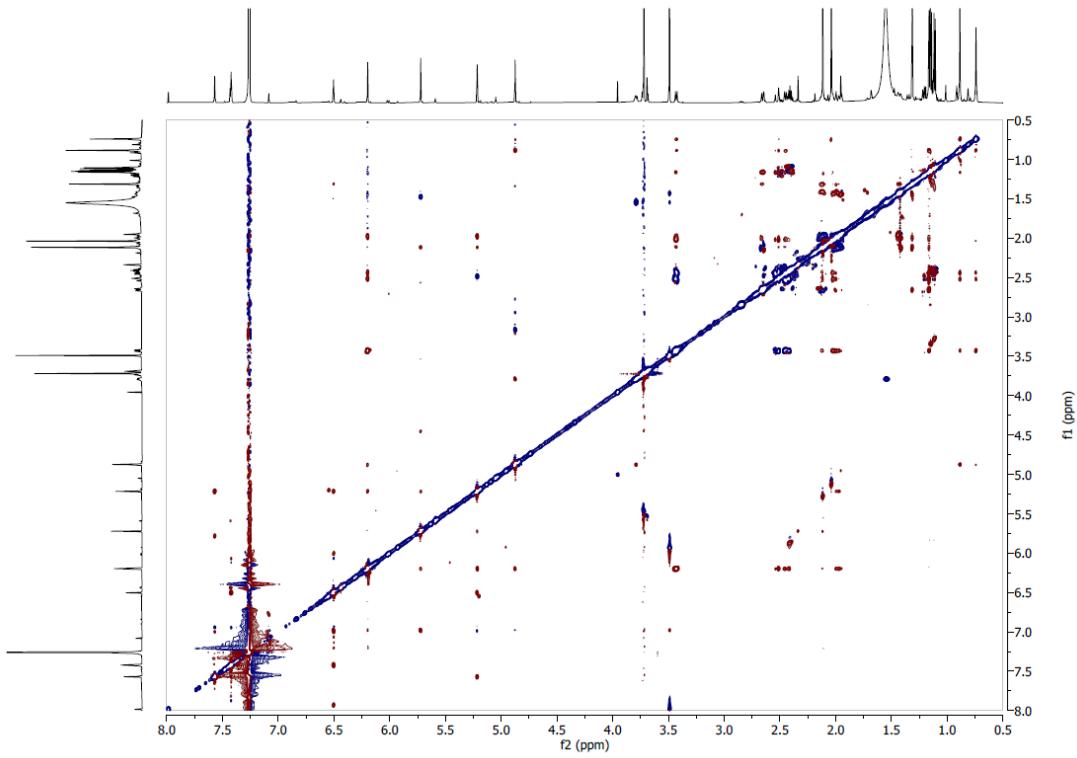
Supplementary Figure S4.2.164. ^{13}C -DEPTQ NMR spectrum of compound **28** in CDCl_3 at 151 MHz



Supplementary Figure S4.2.165. Edited HSQC NMR spectrum of compound **28** in CDCl_3

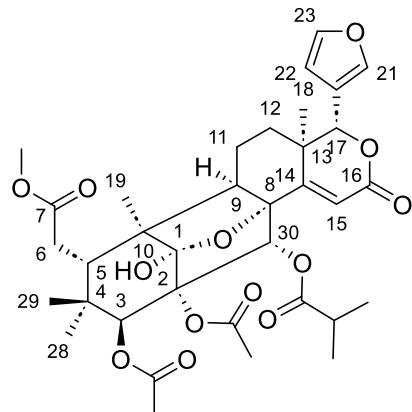


Supplementary Figure S4.2.166. HMBC NMR spectrum of compound **28** in CDCl_3

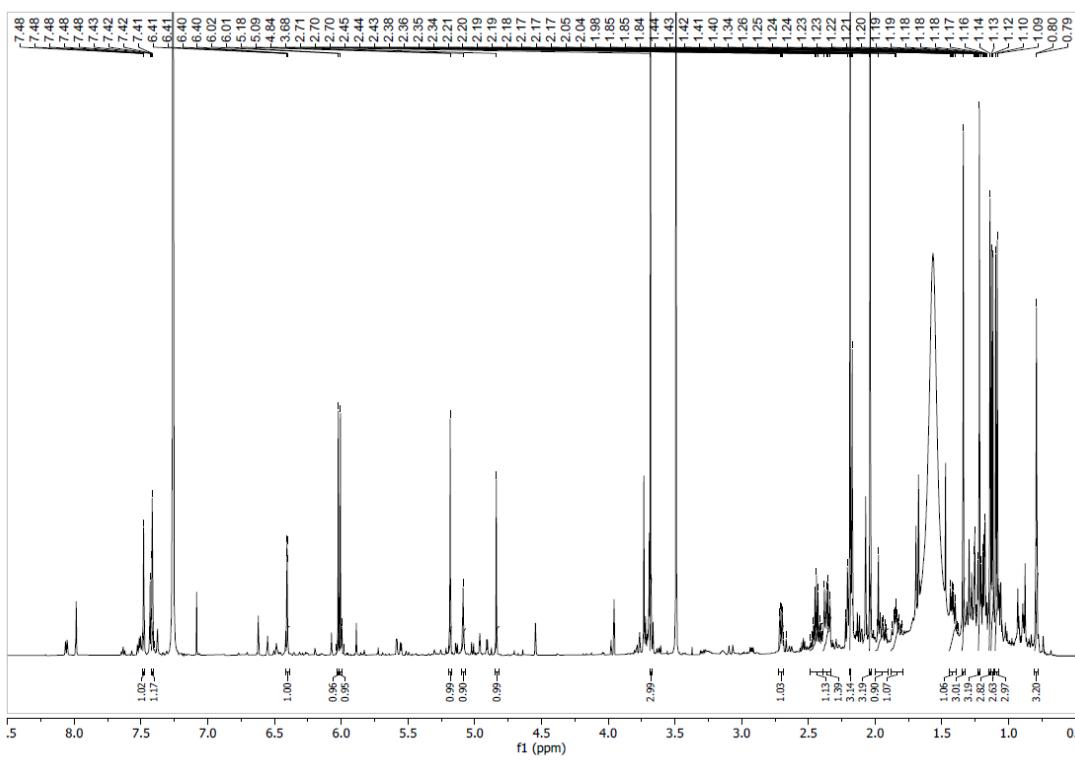


Supplementary Figure S4.2.167. ROESY NMR spectrum of compound **28** in CDCl_3

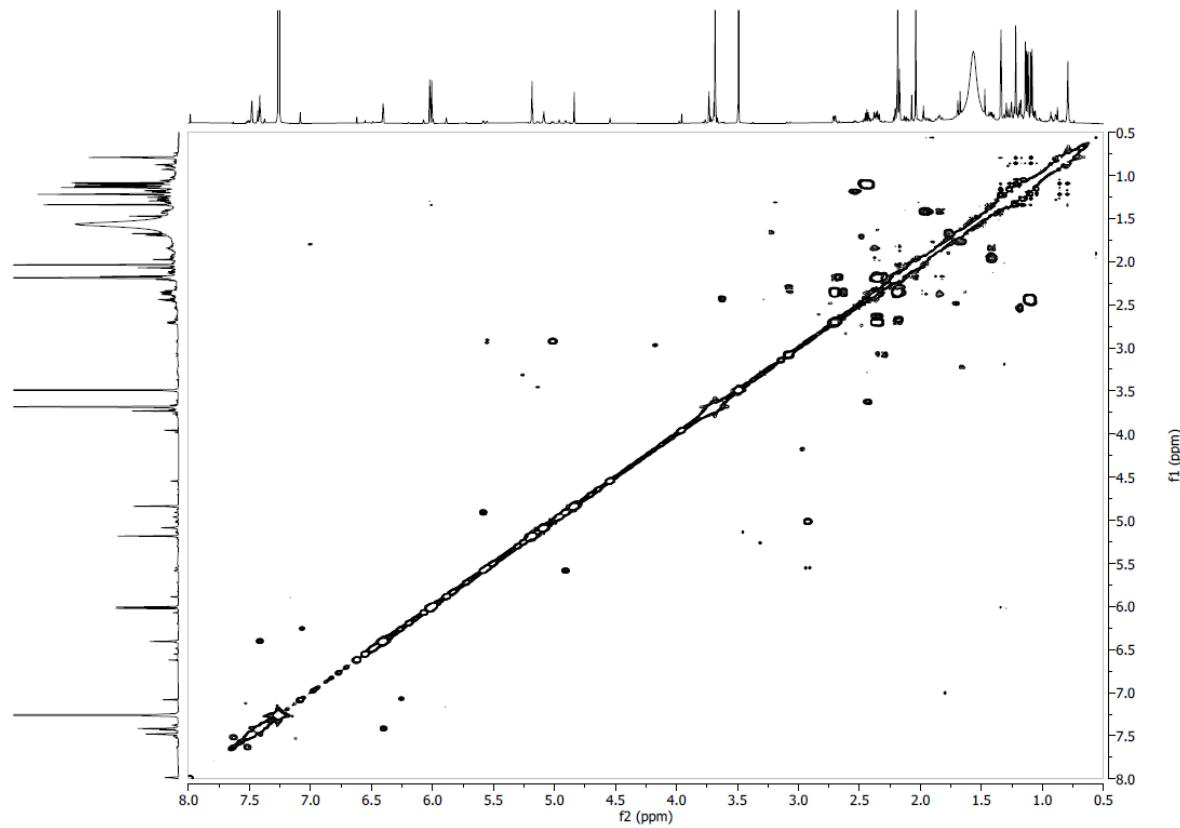
Compound 29: 2-acetyl-utilin C. Amorphous white powder, HRESIMS m/z 673.3956 [M+H]⁺ (calculated for C₃₅H₄₄O₁₃, error 0.25 ppm); $[\alpha]_D^{20} -25$ (c 0.0004 CHCl₃); UV (c 0.004, MeOH) λ_{max} 200, 215 nm.



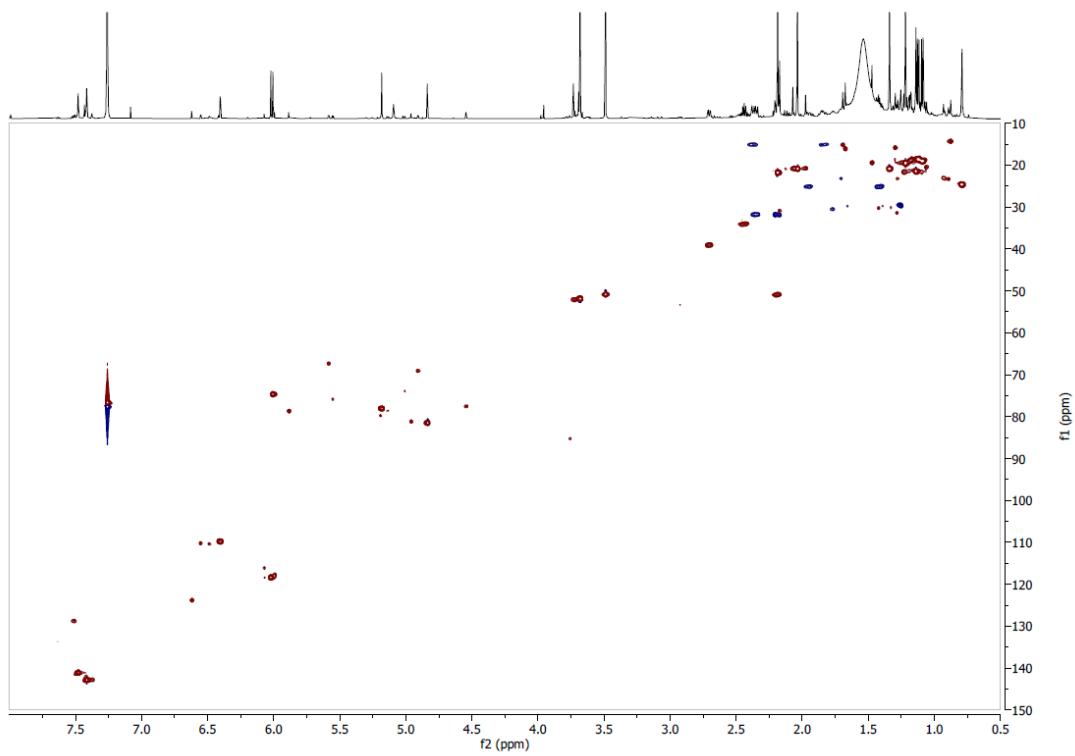
¹H NMR (CDCl₃, 600 MHz) δ 0.79 (3H, s, H₃-29), 1.09 (3H, d, J = 7.0 Hz, H₃-30d), 1.12 (3H, d, J = 7.0 Hz, H₃-30c), 1.14 (3H, s, H₃-19), 1.22 (3H, s, H₃-18), 1.34 (3H, s, H₃-28), 1.42 (1H, dd, J = 13.9, 8.4 Hz, H-12a), 1.85 (1H, m, H-11a), 1.95 (1H, m, H-12b), 2.04 (3H, s, H₃-2b), 2.19 (3H, s, H₃-3b), 2.19 (2H, overlapped, H-6'', H-9), 2.36 (1H, dd, J = 16.4, 9.6 Hz, H-6'), 2.37 (1H, overlapped, H-11b), 2.44 (1H, hept, J = 7.0 Hz, H-30b), 2.71 (1H, dd, J = 9.6, 2.6 Hz, H-5), 3.68 (3H, s, OCH₃), 4.84 (1H, s, H-17), 5.09 (1H, s, OH-1), 5.18 (1H, s, H-3), 6.01 (1H, s, H-30), 6.02 (1H, s, H-15), 6.41 (1H, t, J = 1.7, 0.9 Hz, H-22), 7.42 (1H, t, J = 1.7 Hz, H-23), 7.48 (1H, t, J = 1.7, 0.9 Hz, H-21); ¹³C NMR (CDCl₃, 151 MHz) δ 15.1 (CH₂-11), 18.6 (CH₃-30c), 19.0 (CH₃-30d), 19.4 (CH₃-18), 20.8 (CH₃-28, CH₃-2b), 21.4 (CH₃-19), 21.7 (CH₃-3b), 24.5 (CH₃-29), 25.1 (CH₂-12), 31.8 (CH₂-6), 34.1 (CH-30b), 38.9 (C-13), 39.0 (CH-5), 39.6 (C-4), 43.4 (C-10), 50.9 (CH-9), 52.0 (OCH₃), 74.7 (CH-30), 78.1 (CH-3), 80.4 (C-8), 81.5 (CH-17), 90.1 (C-2), 108.1 (C-1), 109.8 (CH-22), 118.4 (CH-15), 119.8 (C-20), 141.1 (CH-21), 142.9 (CH-23), 158.2 (C-14), 163.1 (C-16), 170.1 (C-2a, C-3a), 173.7 (C-7), 175.3 (C-30a). **Supplementary Figures S4.2.168-S4.2.172.**



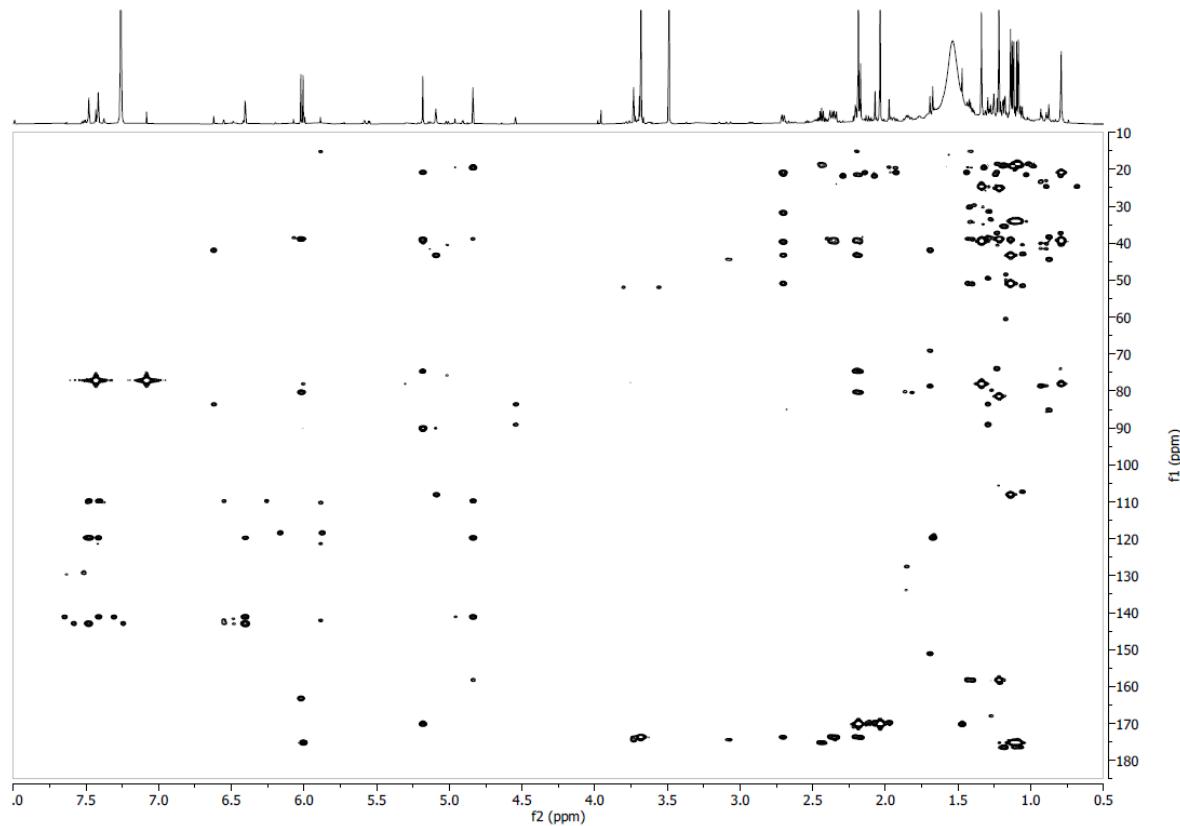
Supplementary Figure S4.2.168. ^1H NMR spectrum of compound **29** in CDCl_3 at 600 MHz



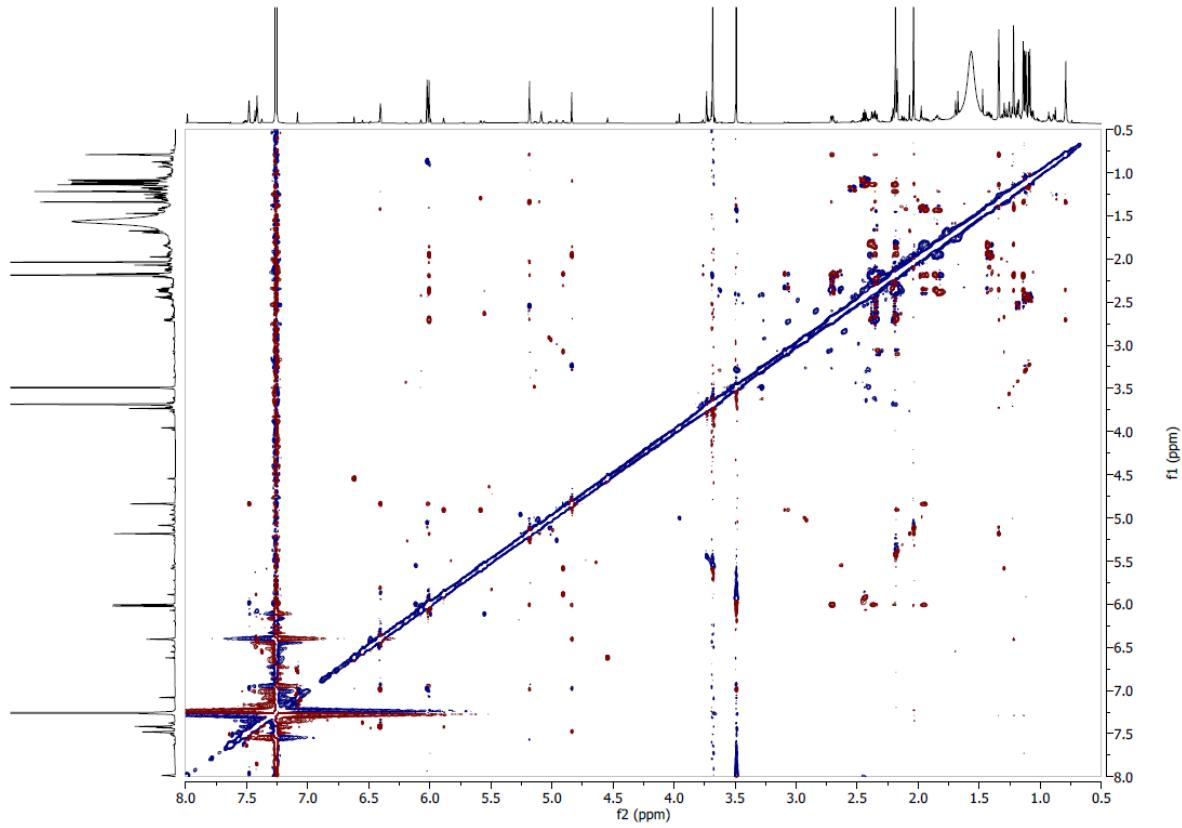
Supplementary Figure S4.2.16. COSY NMR spectrum of compound **29** in CDCl_3



Supplementary Figure S4.2.170. Edited HSQC NMR spectrum of compound **29** in CDCl_3

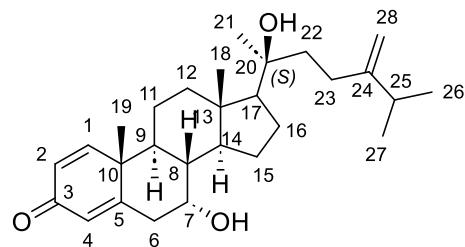


Supplementary Figure S4.2.171. HMBC NMR spectrum of compound **29** in CDCl_3



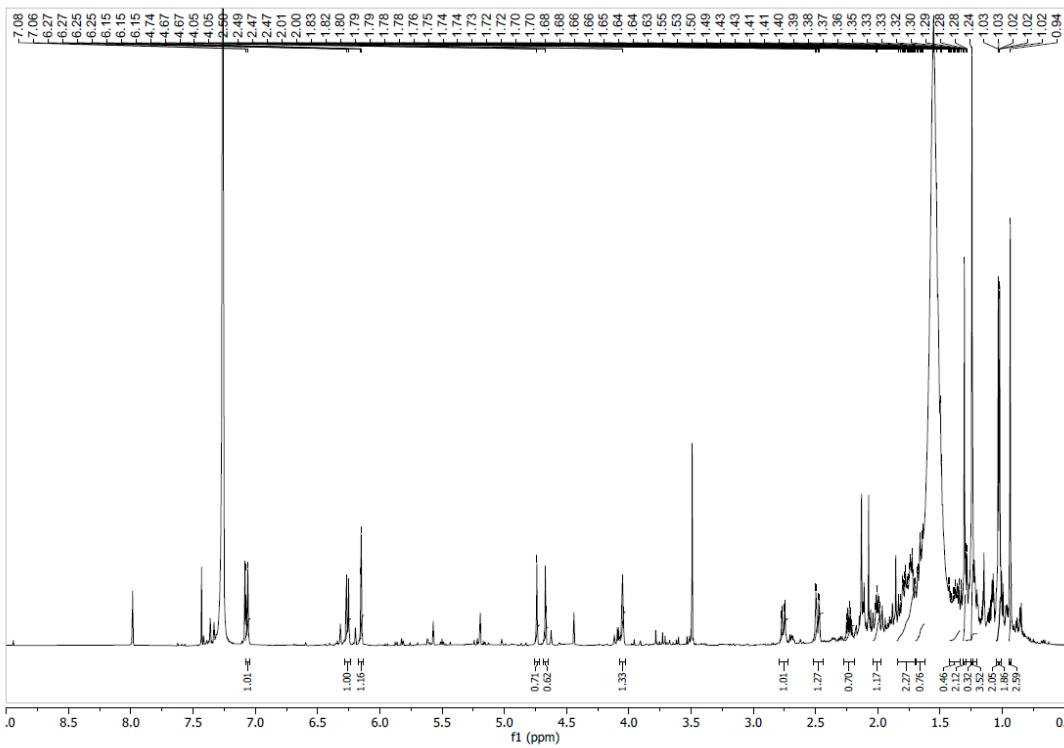
Supplementary Figure S4.2.172. ROESY NMR spectrum of compound **29** in CDCl_3

Compound 30: 7,20-dihydroxy-3-oxo-ergosta-1,4,24-triene. Amorphous white powder, HRESIMS m/z 457.2945 [M+H]⁺ (calculated for C₂₈H₄₁O₅, error -0.33 ppm); $[\alpha]_D^{20}$ -12 (c 0.0002 CHCl₃); UV (c 0.0002, CHCl₃) λ_{max} 185, 201, 247 nm.

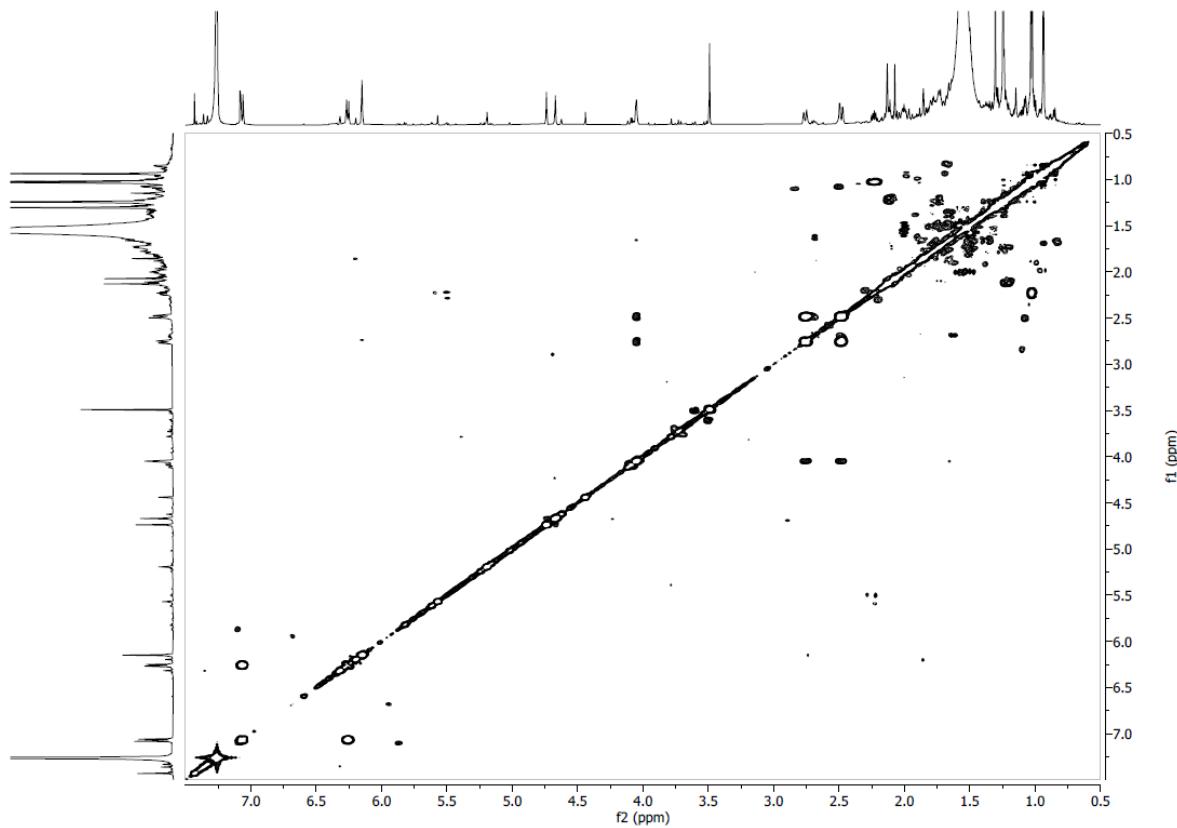


¹H NMR (CDCl₃, 600 MHz) δ 0.94 (3H, s, H₃-18), 1.03 (3H, d, J = 7.0 Hz, H₃-27), 1.03 (3H, d, J = 7.0 Hz, H₃-26), 1.22 (1H, m, H-12a), 1.24 (3H, s, H₃-19), 1.24 (1H, m, H-15''), 1.30 (3H, s, H₃-21), 1.38 (1H, m, H-14), 1.50 (1H, m, H-9), 1.51 (1H, m, H-22''), 1.52 (1H, m, H-17), 1.58 (1H, m, H-22'), 1.66 (1H, td, J = 11.3, 2.6 Hz, H-8), 1.73 (3H, m, H₂-11, H-16''), 1.76 (1H, m, H-15'), 1.80 (1H, m, H-16'), 2.01 (2H, m, H₂-23), 2.11 (1H, m, H-12b), 2.23 (1H, hept, J = 7.0 Hz, H-25), 2.48 (1H, dd, J = 13.9, 2.8 Hz, H-6 α), 2.76 (1H, dt, J = 13.9, 3.2, 1.8 Hz, H-6 β), 4.05 (1H, q, J = 3.2, 2.8 Hz, H-7), 4.67 (1H, q, J = 1.4 Hz, H-28''), 4.74 (1H, s, H-28'), 6.15 (1H, t, J = 1.8 Hz, H-4), 6.26 (1H, dd, J = 10.2, 1.8 Hz, H-2), 7.07 (1H, d, J = 10.2 Hz, H-1); ¹³C NMR (CDCl₃, 151 MHz) δ 13.5 (CH₃-18), 18.2 (CH₃-19), 21.9 (CH₃-26, CH₃-27), 22.3 (CH₂-11, CH₂-16), 23.2 (CH₂-15), 26.3 (CH₃-21), 28.9 (CH₂-23), 34.0 (CH-25), 39.1 (CH-8), 39.3 (CH₂-12), 40.9 (CH₂-6), 42.5 (CH₂-22), 42.9 (C-13), 43.4 (C-10), 44.4 (CH-9), 50.4 (CH-14), 57.6 (CH-17), 69.5 (CH-7), 74.8 (C-20), 106.3 (CH₂-28), 127.2 (CH-4), 127.8 (CH-2), 155.4 (CH-1), 155.9 (C-24), 164.3 (C-5), 185.6 (C-3).

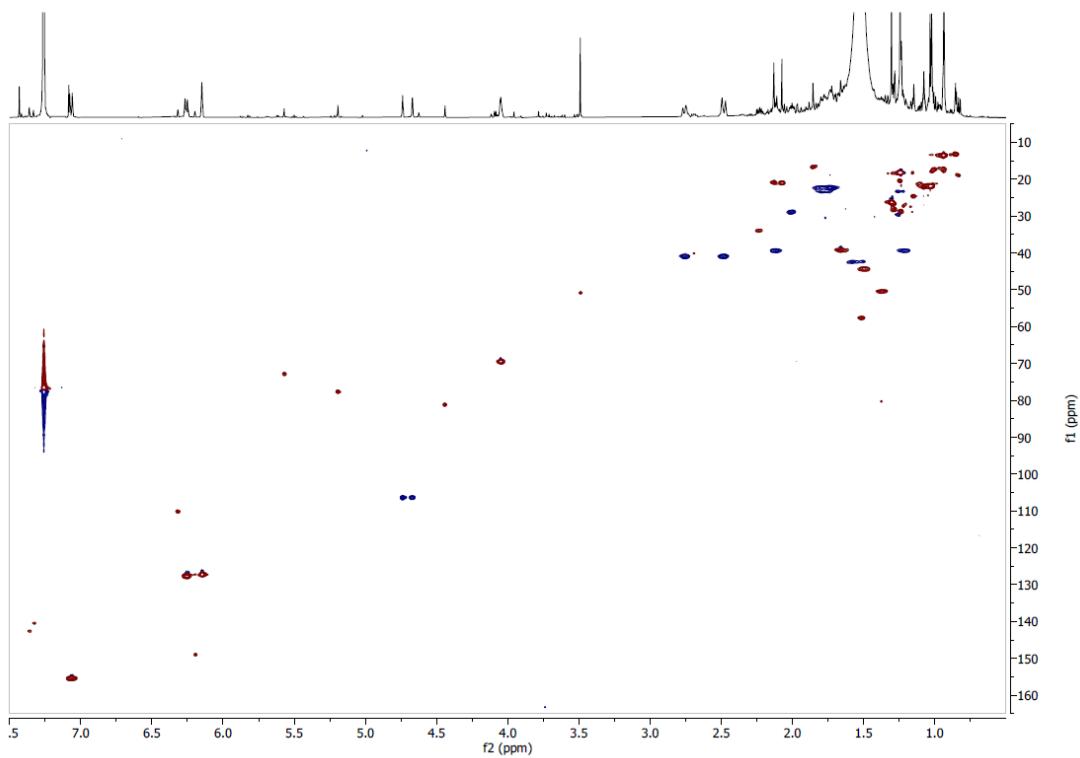
Supplementary Figures S4.2.173-S4.2.177.



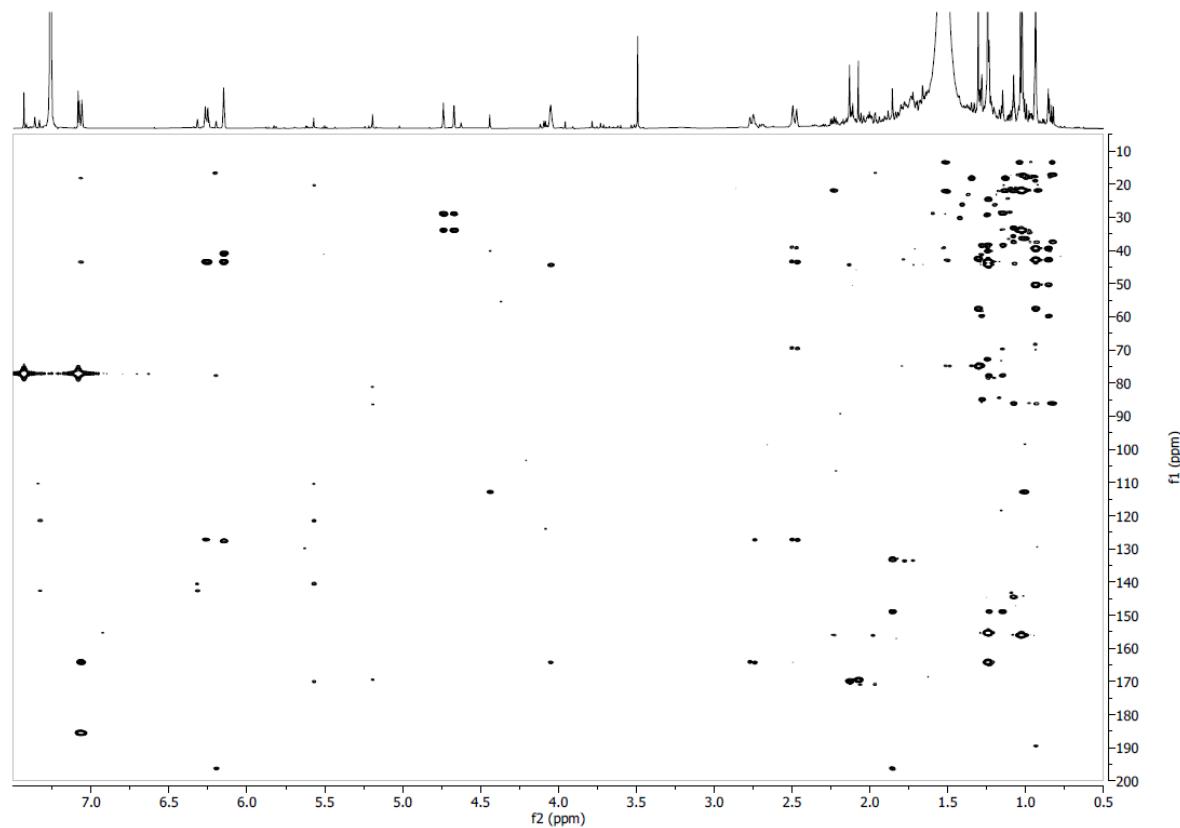
Supplementary Figure S4.2.173. ¹H NMR spectrum of compound **30** in CDCl_3 at 600 MHz



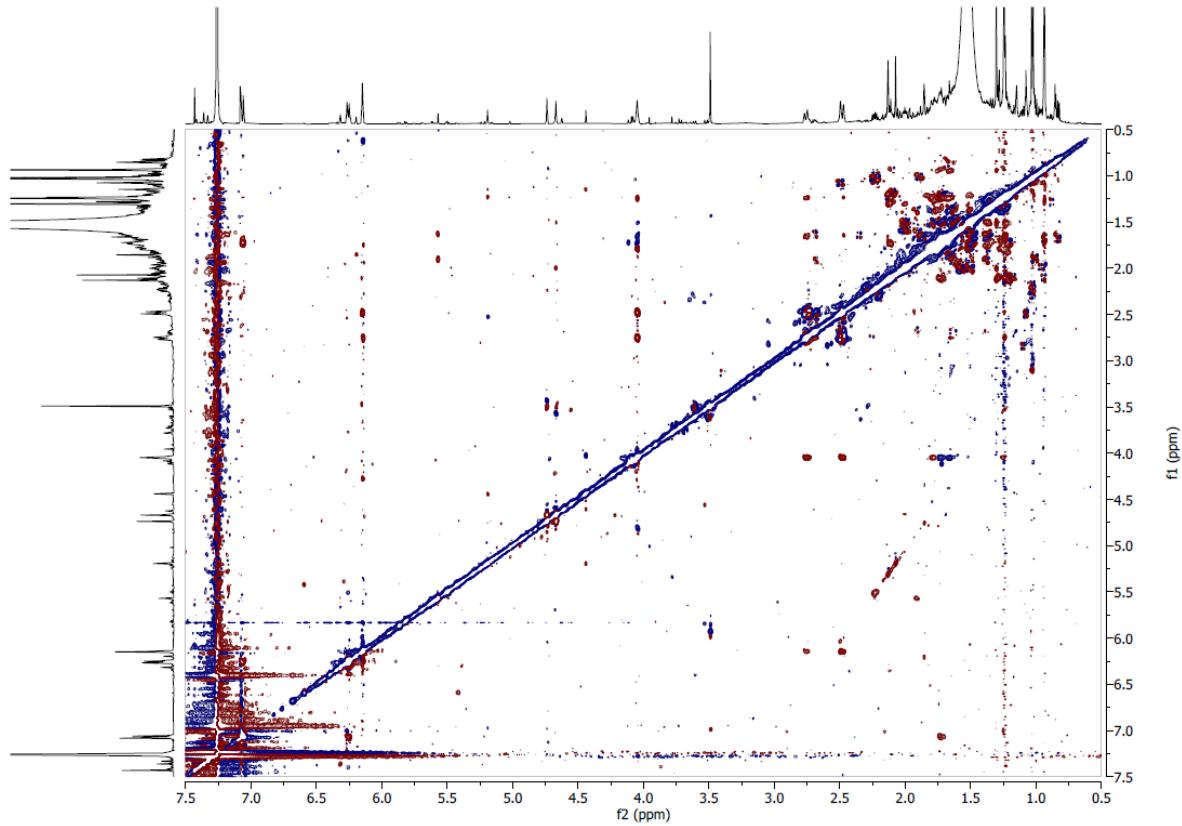
Supplementary Figure S4.2.174. COSY NMR spectrum of compound **30** in CDCl_3



Supplementary Figure S4.2.175. Edited HSQC NMR spectrum of compound **30** in CDCl_3

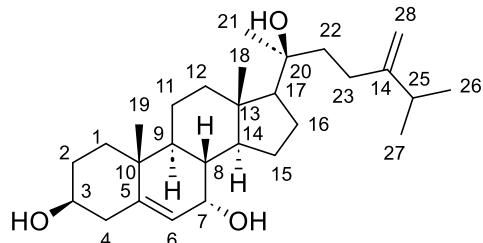


Supplementary Figure S4.2.176. HMBC NMR spectrum of compound **30** in CDCl_3

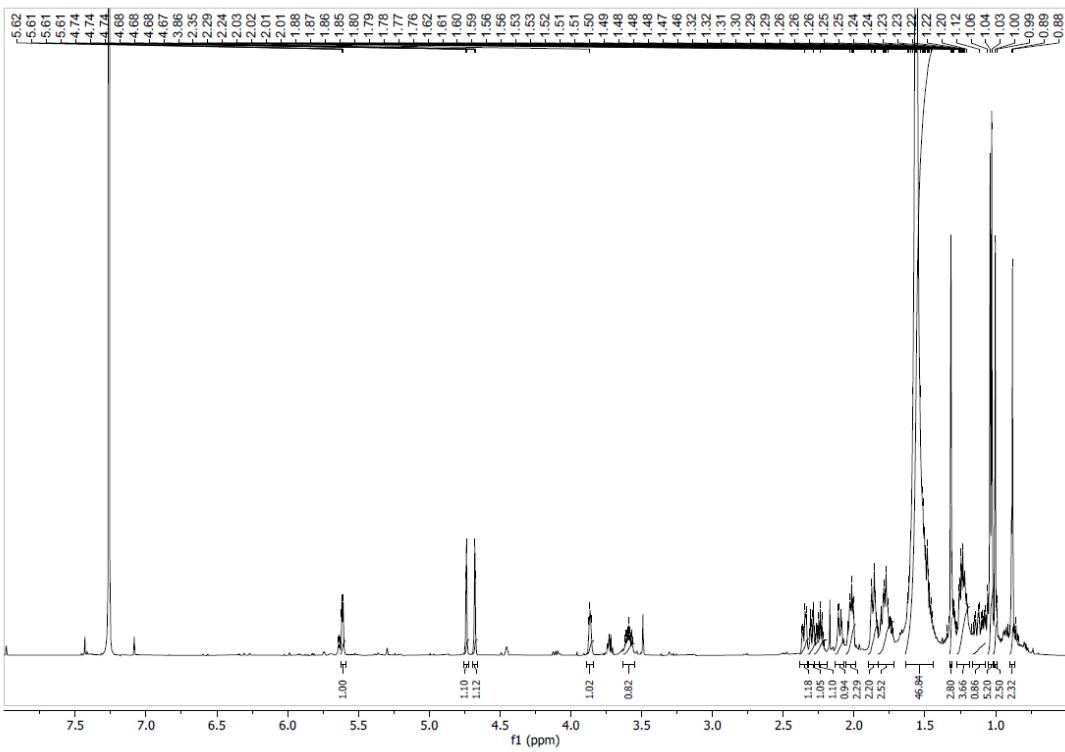


Supplementary Figure S4.2.177. ROESY NMR spectrum of compound **30** in CDCl_3

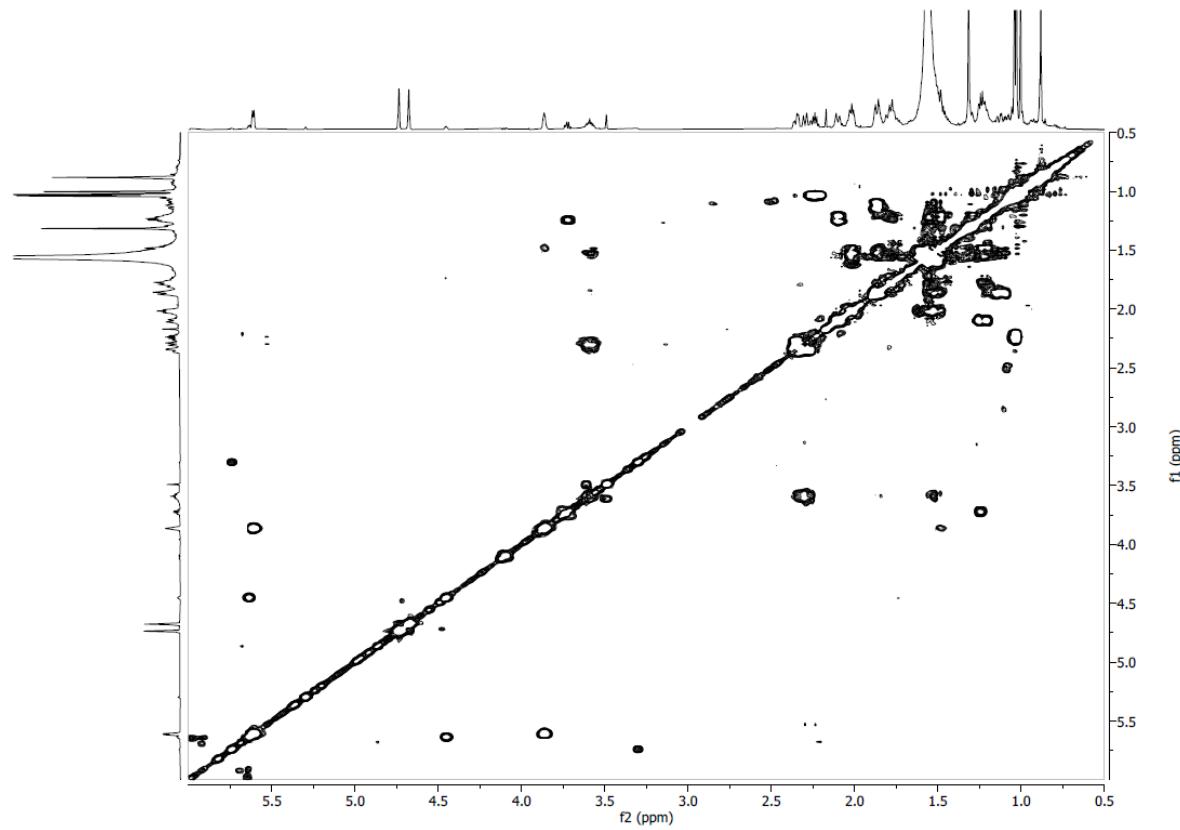
Compound 31: 3,7,20-trihydroxyergosta-5,24(28)-diene. Amorphous white powder, HRESIMS m/z 687.2610 [M+Na]⁺ (calculated for C₃₃H₄₄O₁₄Na, error -0.97 ppm), 663.2657 [M-H]⁻ (calculated for C₃₃H₄₃O₁₄, error 1.53 ppm); $[\alpha]_D^{20}$ -0.95 (c 0.0004 CHCl₃); UV (c 0.004, MeOH) λ_{max} 210, 251 nm.



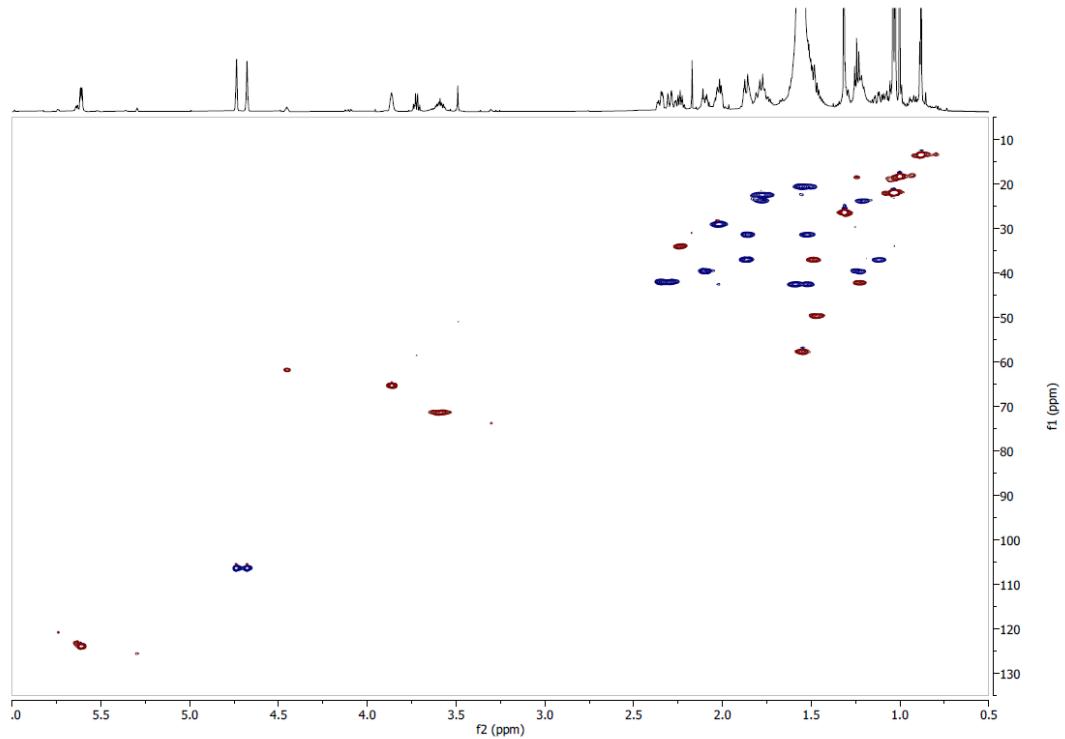
¹H NMR (CDCl₃, 600 MHz) δ 0.88 (3H, s, H₃-18), 1.00 (3H, s, H₃-19), 1.03 (6H, d, J = 6.9 Hz, H₃-26, H₃-27), 1.12 (1H, td, J = 14.9, 13.9, 4.1 Hz, H-1 α), 1.24 (3H, m, H-9, H-12a, H-15 $''$), 1.32 (3H, s, H₃-21), 1.47 (1H, m, H-14), 1.49 (1H, m, H-8), 1.52 (2H, m, H-2 $''$, H-22 $''$), 1.55 (3H, m, H-17, H₂-11), 1.59 (1H, m, H-22'), 1.77 (3H, m, H-15', H₂-16), 1.86 (2H, m, H-1 β , H-2'), 2.02 (2H, m, H₂-23), 2.10 (1H, dt, J = 12.3, 3.1 Hz, H-12b), 2.24 (1H, hept, J = 6.9 Hz, H-25), 2.29 (1H, td, J = 13.0, 11.2, 1.5 Hz, H-4 β), 2.35 (1H, dt, J = 13.0, 4.6, 1.5 Hz, H-4 α), 3.59 (1H, tt, J = 11.2, 4.6 Hz, H-3), 3.86 (1H, t, J = 4.8 Hz, H-7), 4.68 (1H, brs, H-28 $''$), 4.74 (1H, brs, H-28'), 5.61 (1H, dt, J = 4.8, 1.5 Hz, H-6); ¹³C NMR (CDCl₃, 600 MHz) δ 13.3 (CH₃-18), 18.3 (CH₃-19), 20.5 (CH₂-11), 21.9 (CH₃-26, CH₃-27), 22.4 (CH₂-16), 23.8 (CH₂-15), 26.3 (CH₃-21), 29.0 (CH₂-23), 31.4 (CH₂-2), 33.9 (CH-25), 36.9 (CH-8, CH₂-1), 37.6 (C-10), 39.5 (CH₂-12), 42.0 (CH₂-4), 42.2 (CH-9), 42.5 (CH₂-22), 49.6 (CH-14), 57.6 (CH-17), 65.2 (CH-7), 71.4 (CH-3), 75.1 (C-20), 106.4 (CH₂-28), 123.9 (CH-6), 146.3 (C-5), 156.2 (C-24). **Supplementary Figures S4.2.178-S4.2.182.**



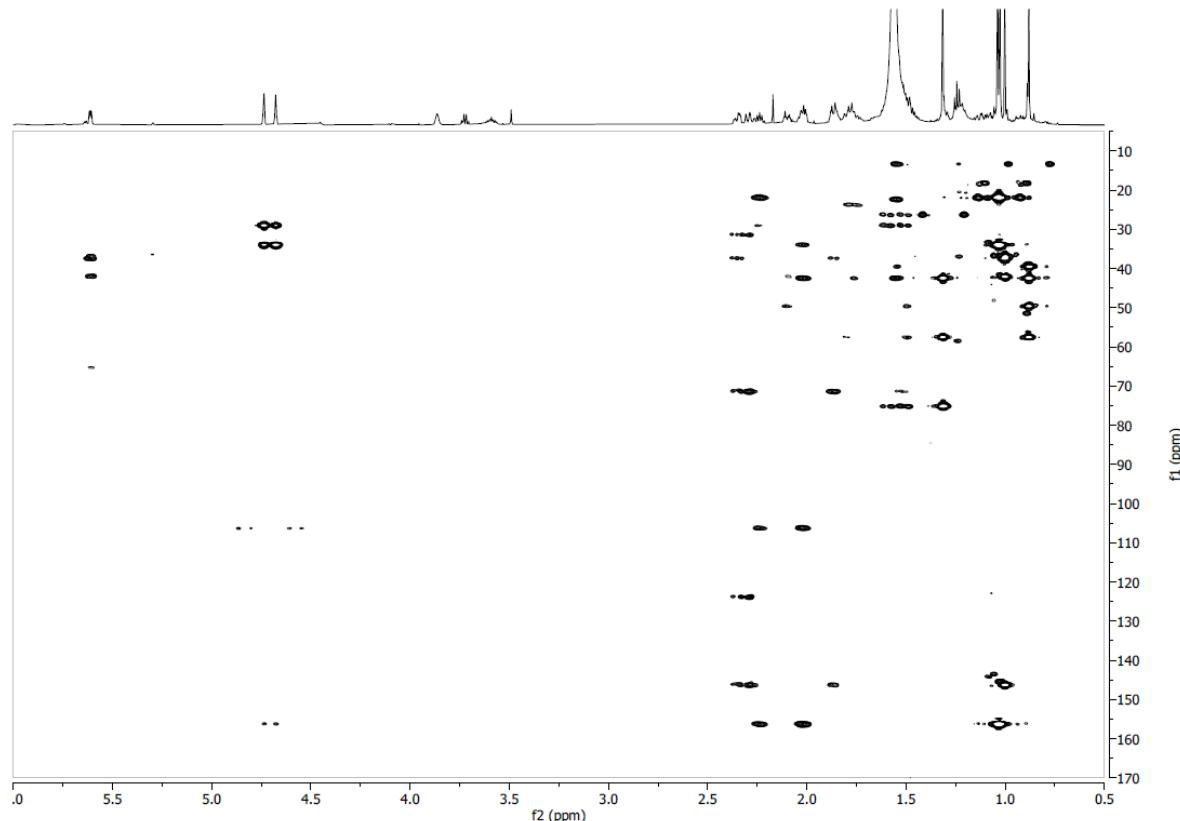
Supplementary Figure S4.2.178. ^1H NMR spectrum of compound 31 in CDCl_3 at 600 MHz



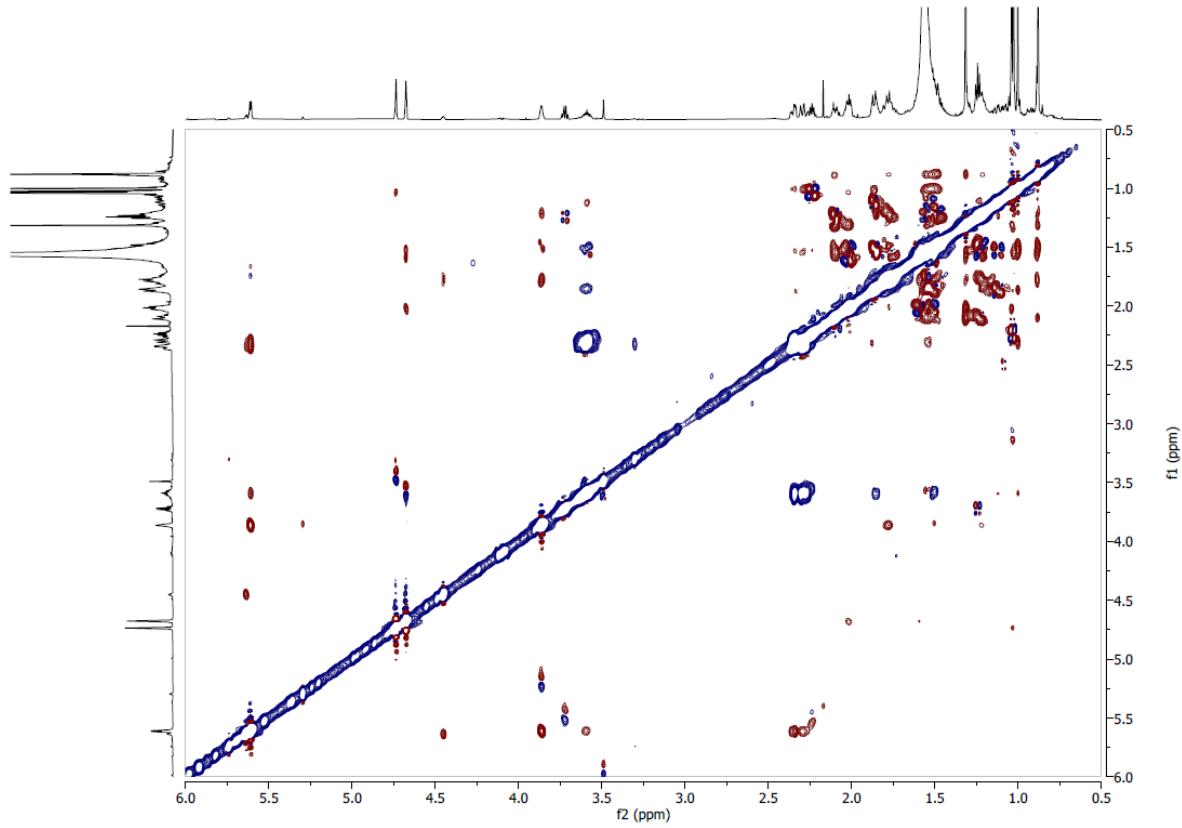
Supplementary Figure S4.2.179. COSY NMR spectrum of compound 31 in CDCl_3



Supplementary Figure S4.2.180. Edited HSQC NMR spectrum of compound **31** in CDCl_3

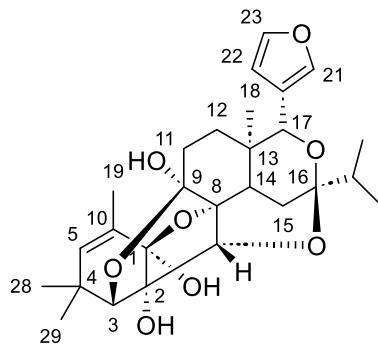


Supplementary Figure S4.2.181. HMBC NMR spectrum of compound **31** in CDCl_3

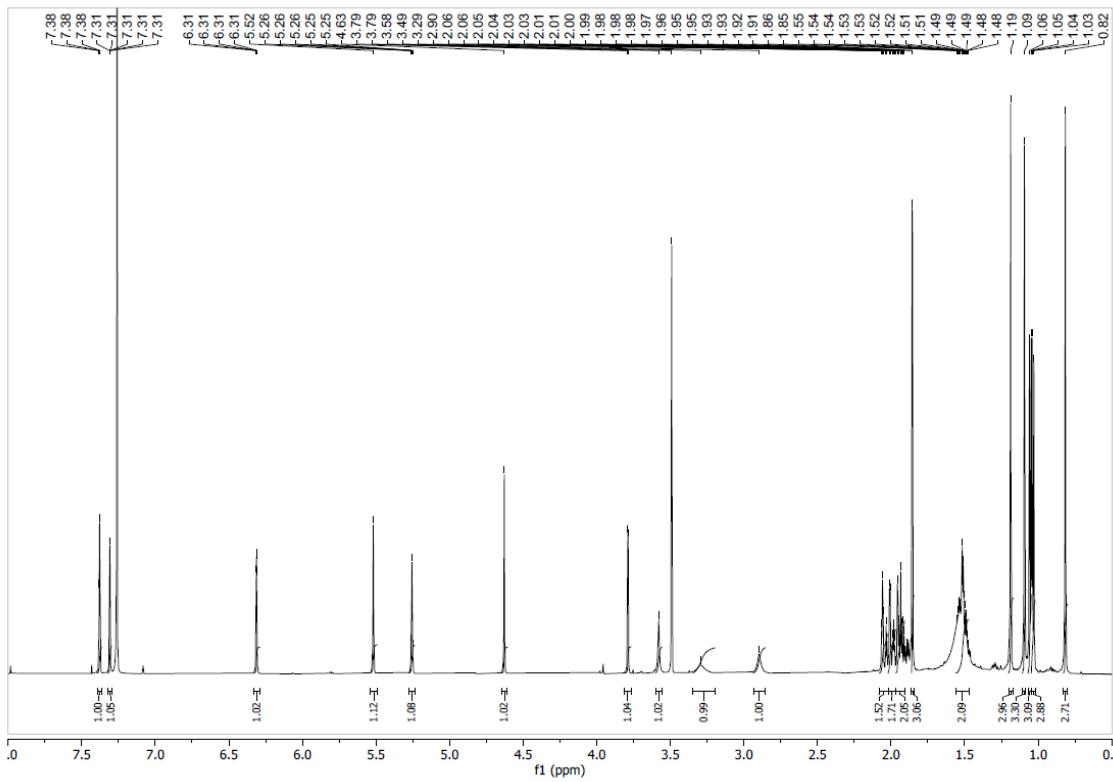


Supplementary Figure S4.2.182. ROESY NMR spectrum of compound **31** in CDCl_3

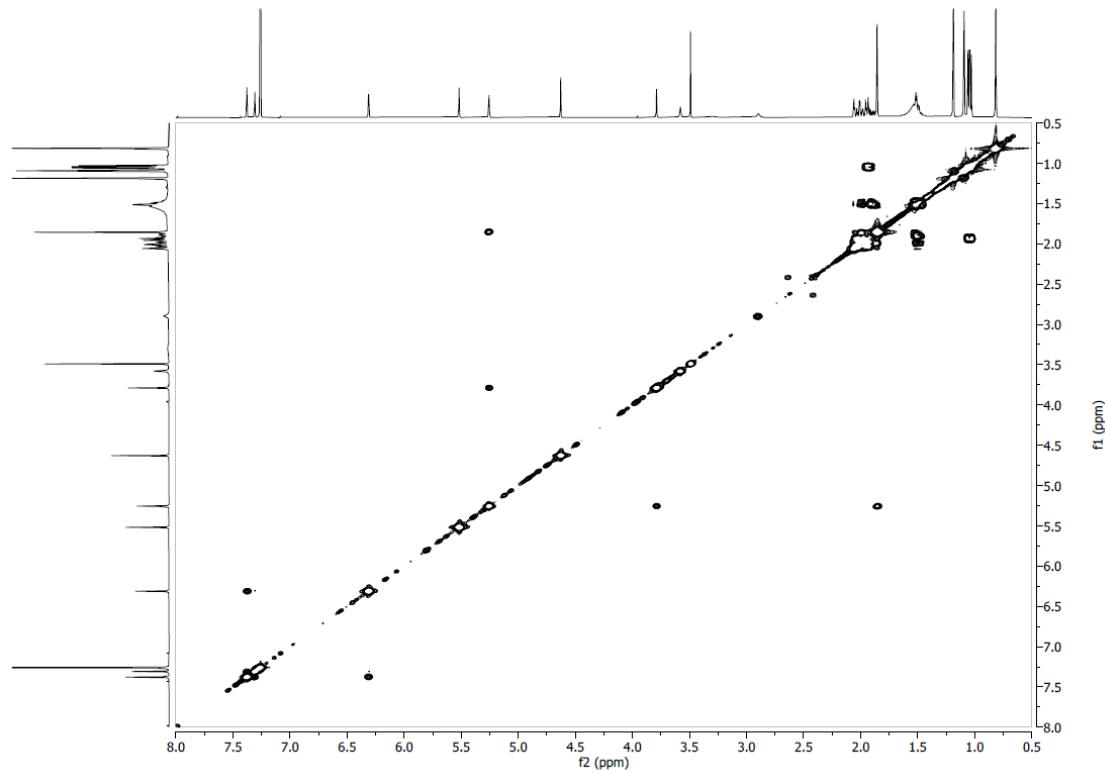
Compound **32**: Entilin A [82]. Amorphous white powder, HRESIMS m/z 487.2336 [$M-H^-$] (calculated for $C_{27}H_{36}O_8$, error 2.1 ppm); $[\alpha]_D^{20} -14$ (c 0.002 CHCl₃); UV (c 0.002, CHCl₃) λ_{max} 198, 215 nm.



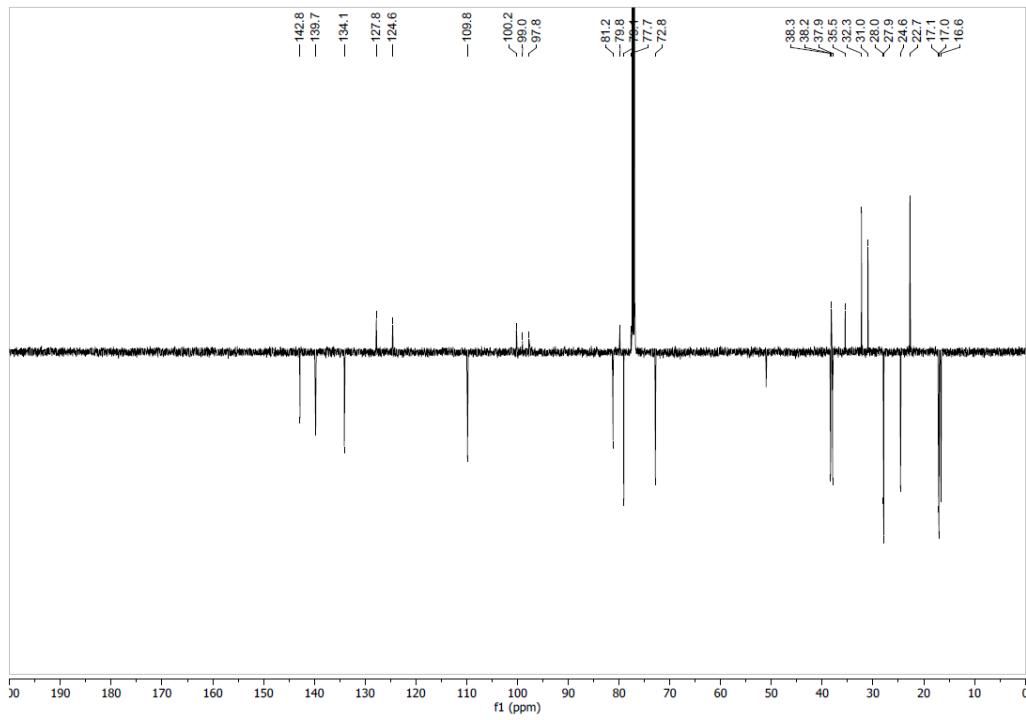
¹H NMR (CDCl₃, 600 MHz) δ 0.82 (3H, s, H₃-18), 1.03 (3H, d, J = 6.9 Hz, H₃-15d), 1.05 (3H, d, J = 7.0 Hz, H₃-15c), 1.09 (3H, s, H₃-29b), 1.19 (3H, s, H₃-28a), 1.51 (2H, m, H₂-12), 1.86 (3H, d, J = 1.5 Hz, H₃-19), 1.89 (1H, m, H-11b), 1.94 (2H, m, H-15a, H-15b), 1.99 (2H, m, H-11a), 2.02 (1H, m, H-15b), 2.06 (1H, m, H-14), 2.90 (1H, s, OH-2), 3.29 (1H, s, OH-9), 3.58 (1H, s, OH-1), 3.79 (1H, d, J = 1.5 Hz, H-3), 4.63 (1H, s, H-30), 5.26 (1H, p, J = 1.5 Hz, H-5), 5.52 (1H, s, H-17), 6.31 (1H, t, J = 1.8, 0.9 Hz, H-22), 7.31 (1H, t, J = 1.8, 0.9 Hz, H-21), 7.38 (1H, t, J = 1.8 Hz, H-23); ¹³C NMR (CDCl₃, 151 MHz) δ 16.6 (CH₃-19), 17.0 (CH₃-15d), 17.1 (CH₃-15c), 22.7 (CH₂-15), 24.6 (CH₃-18), 27.9 (CH₃-28), 28.0 (CH₃-29), 31.0 (CH₂-11), 32.3 (CH₂-12), 35.5 (C-13), 37.9 (CH-15b), 38.2 (C-4), 38.3 (CH-14), 72.8 (CH-17), 77.7 (C-2), 79.1 (CH-30), 79.8 (C-8), 81.2 (CH-3), 97.8 (C-9), 99.0 (C-1), 100.2 (C-15a), 109.8 (CH-22), 124.6 (C-20), 127.8 (C-10), 134.1 (CH-5), 139.7 (CH-21), 142.8 (CH-23). Supplementary Figures S4.2.183-S4.2.188.



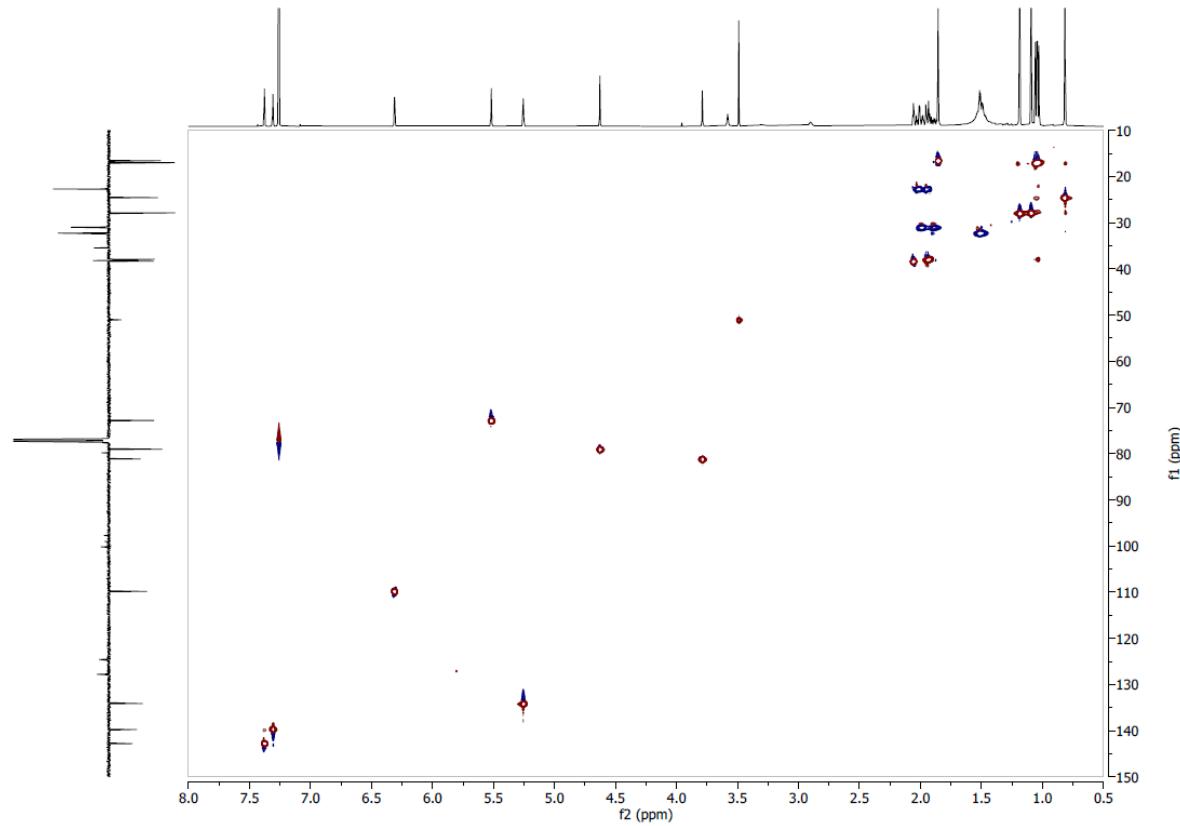
Supplementary Figure S4.2.183. ^1H NMR spectrum of compound **32** in CDCl_3 at 600 MHz



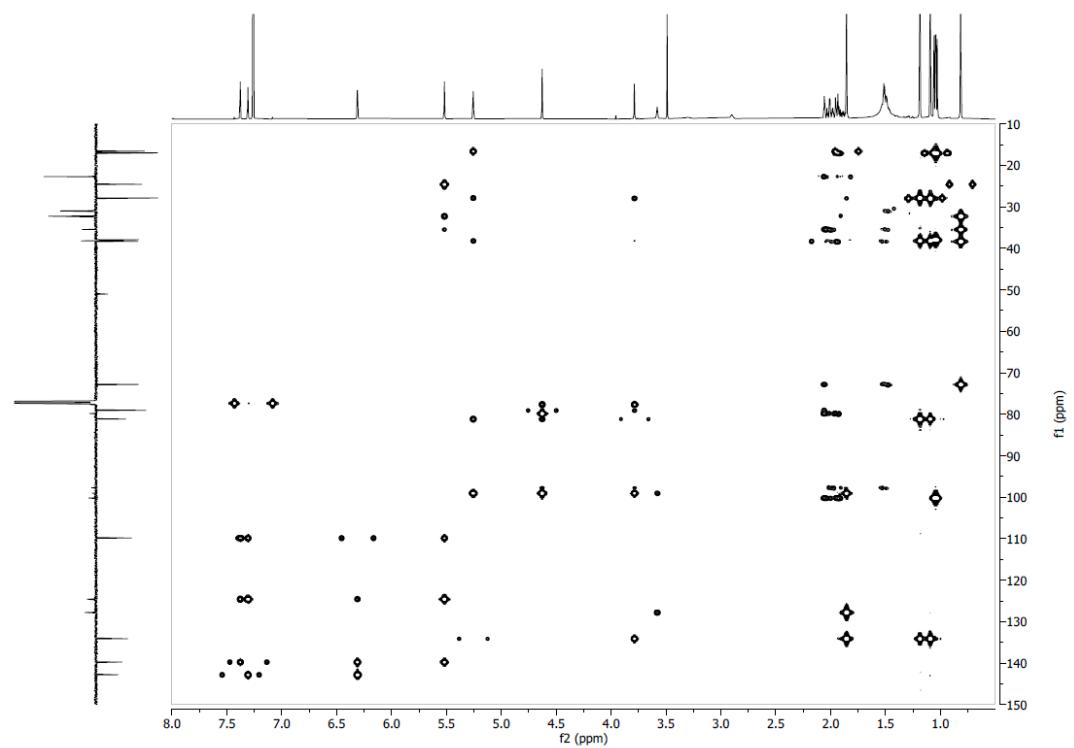
Supplementary Figure S4.2.184. COSY NMR spectrum of compound **32** in CDCl_3



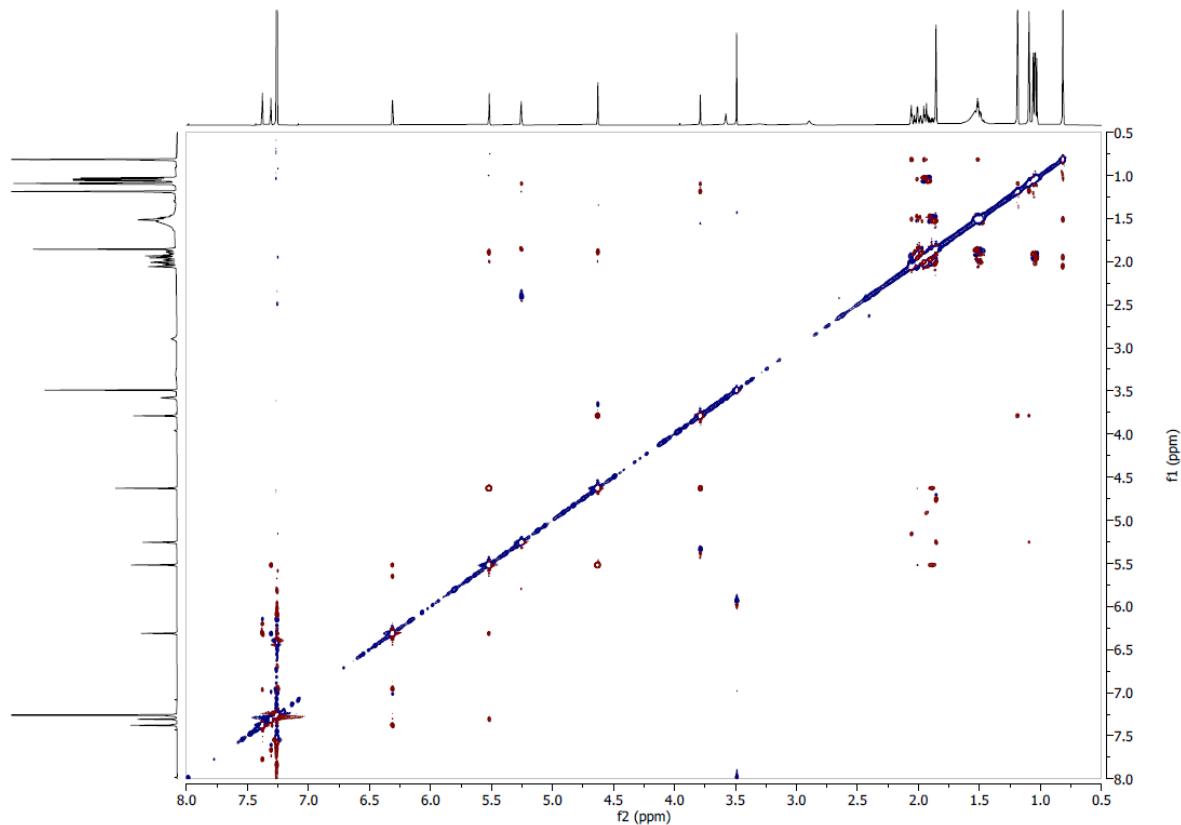
Supplementary Figure S4.2.185. ^{13}C -DEPTQ NMR spectrum of compound **32** in CDCl_3 at 151 MHz



Supplementary Figure S4.2.186. Edited HSQC NMR spectrum of compound **32** in CDCl_3

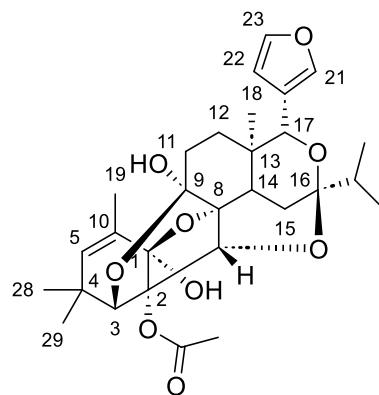


Supplementary Figure S4.2.187. HMBC NMR spectrum of compound **32** in CDCl_3



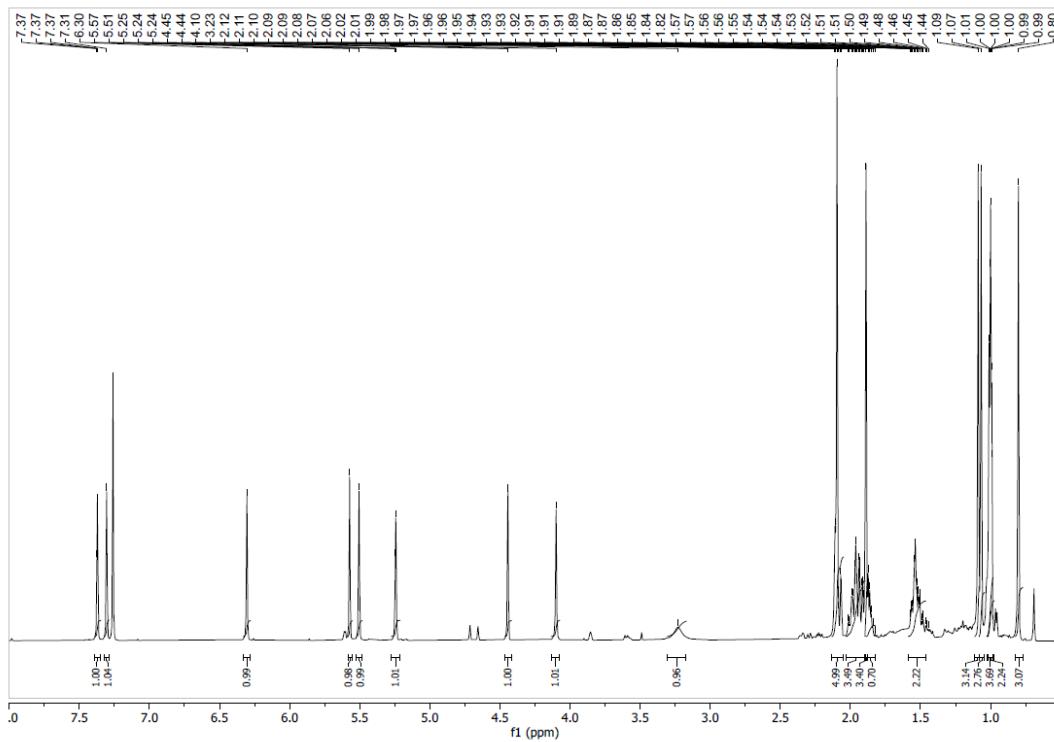
Supplementary Figure S4.2.188. ROESY NMR spectrum of compound **32** in CDCl_3

Compound 33: Entilin B [82]. Amorphous white powder, HRESIMS m/z 531.2595 [$M+H$]⁺ (calculated for C₂₉H₃₈O₉, error 1.24 ppm); $[\alpha]_D^{20} -0.3$ (c 0.004 CHCl₃); UV (c 0.004, CHCl₃) λ_{max} 200, 215 nm.

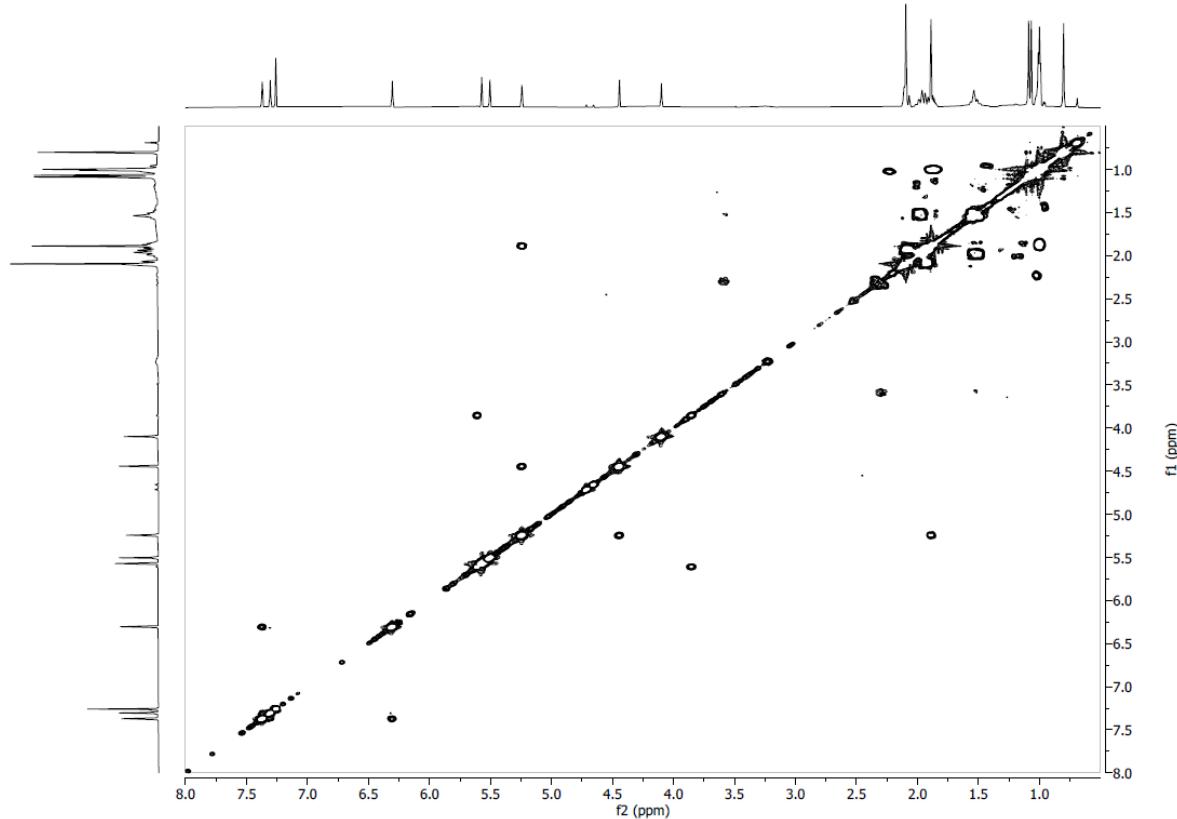


¹H NMR (CDCl₃, 600 MHz) δ 0.80 (3H, s, H₃-18), 1.00 (3H, d, J = 6.8 Hz, H₃-15d), 1.01 (3H, d, J = 6.8 Hz, H₃-15c), 1.07 (3H, s, H₃-29a), 1.09 (3H, s, H₃-28b), 1.53 (2H, m, H₂-12), 1.86 (1H, m, H-15b), 1.89 (3H, s, H₃-19), 1.95 (1H, m, H-15a), 1.97 (1H, m, H₂-11), 2.08 (1H, m, H-15b), 2.09 (3H, s, H₃-2b), 2.11 (1H, m, H-14), 3.23 (1H, s, OH9-), 4.10 (1H, s, OH-1), 4.44 (1H, d, J = 1.8 Hz, H-3), 5.24 (1H, p, J = 1.8 Hz, H-5), 5.51 (1H, s, H-17), 5.57 (1H, s, H-30), 6.30 (1H, s, H-22), 7.31 (1H, s, H-21), 7.37 (1H, t, J = 1.8 Hz, H-23); ¹³C NMR (CDCl₃, 151 MHz) δ 16.6 (CH₃-19), 16.8 (CH₃-15d), 16.9 (CH₃-15c), 21.6 (CH₃-2b), 23.0 (CH₂-15), 24.8 (CH₃-18), 26.8 (CH₃-29), 27.7 (CH₃-28), 30.4 (CH₂-11), 32.4 (CH₂-12), 35.4 (C-13), 37.9 (C-4), 38.0 (CH-15b), 38.5 (CH-14), 73.0 (CH-17), 75.1 (CH-30), 76.1 (CH-3), 80.9 (C-8), 82.4 (C-2), 98.0 (C-9), 99.5 (C-1), 99.9 (C-15a), 109.9 (CH-22), 124.8 (C-20), 128.7 (C-10), 132.6 (CH-5), 139.8 (CH-21), 142.7 (CH-23), 169.7 (C-2a).

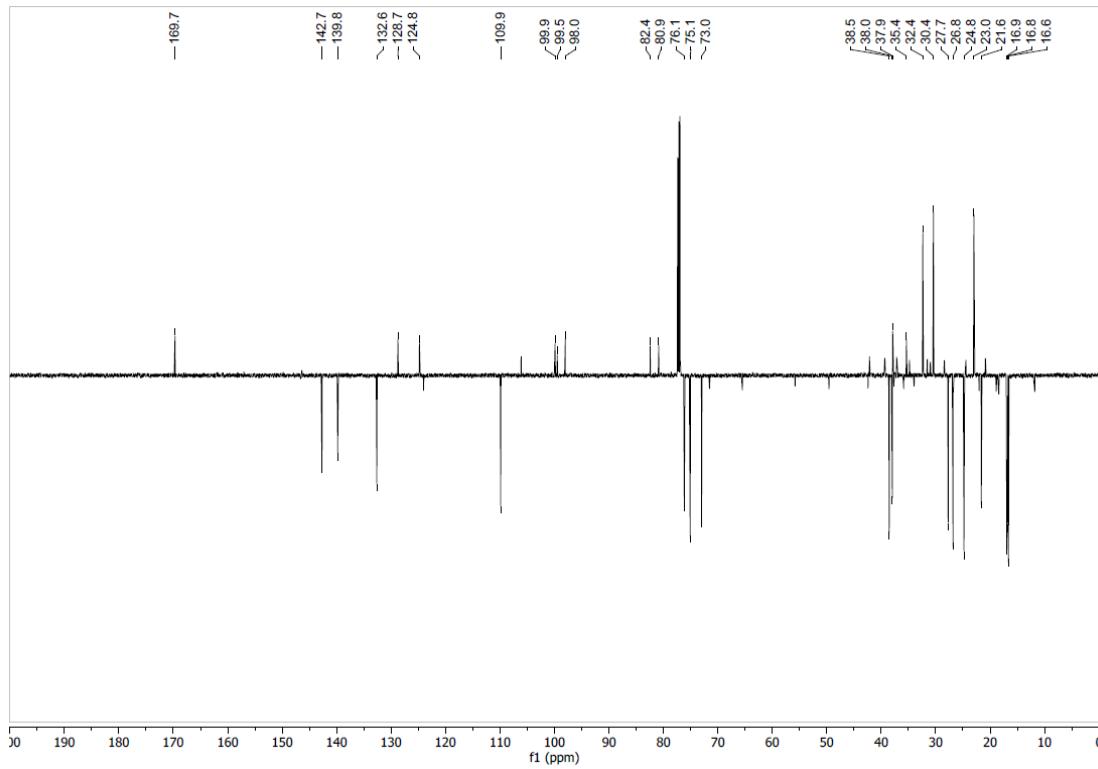
Supplementary Figures S4.2.189-S4.2.194.



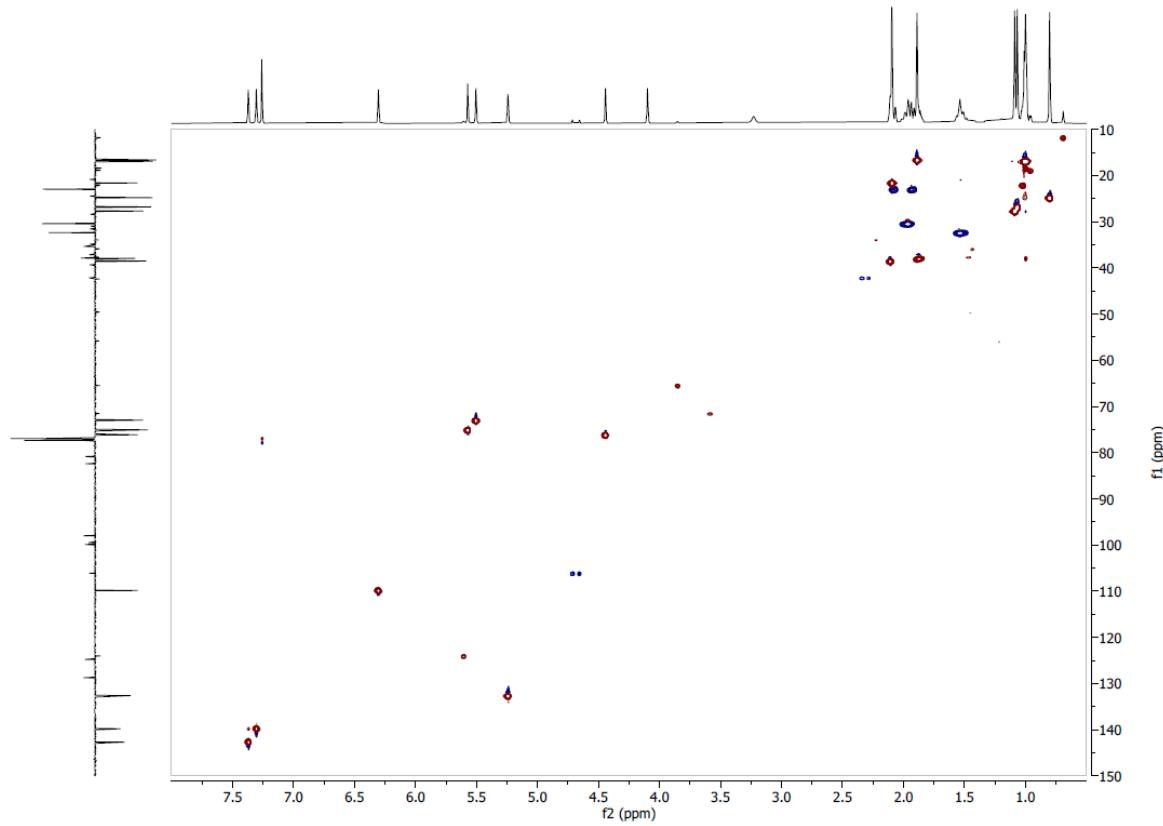
Supplementary Figure S4.2.189. ^1H NMR spectrum of compound **33** in CDCl_3 at 600 MHz



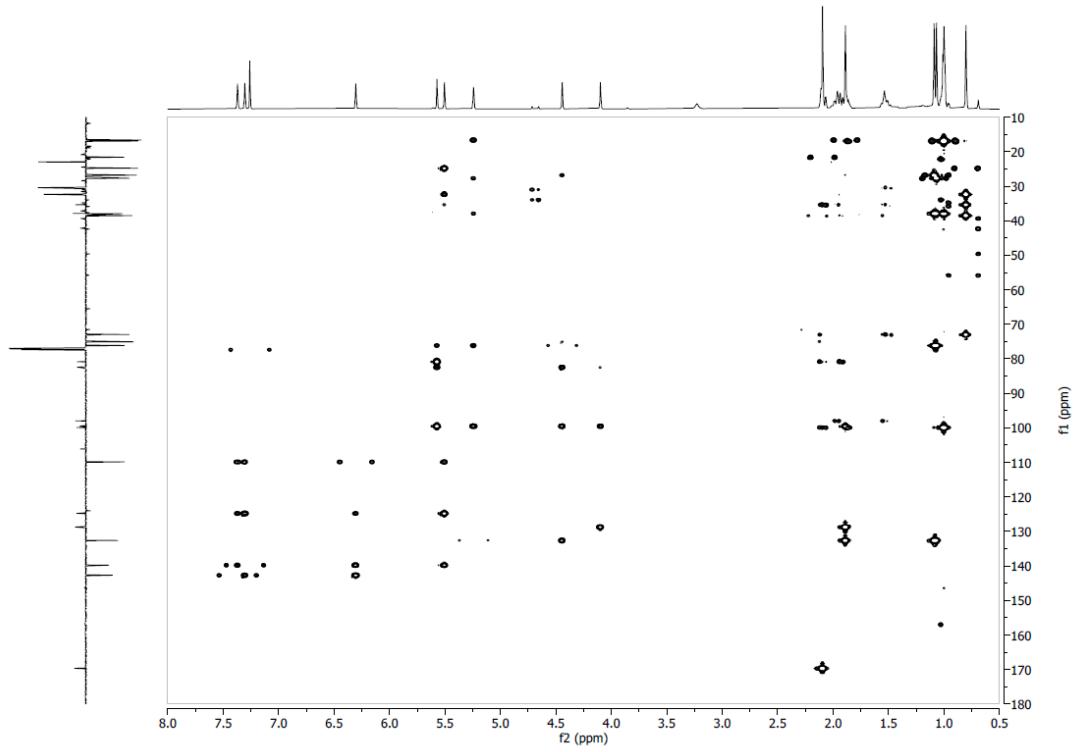
Supplementary Figure S4.2.190. COSY NMR spectrum of compound **33** in CDCl_3



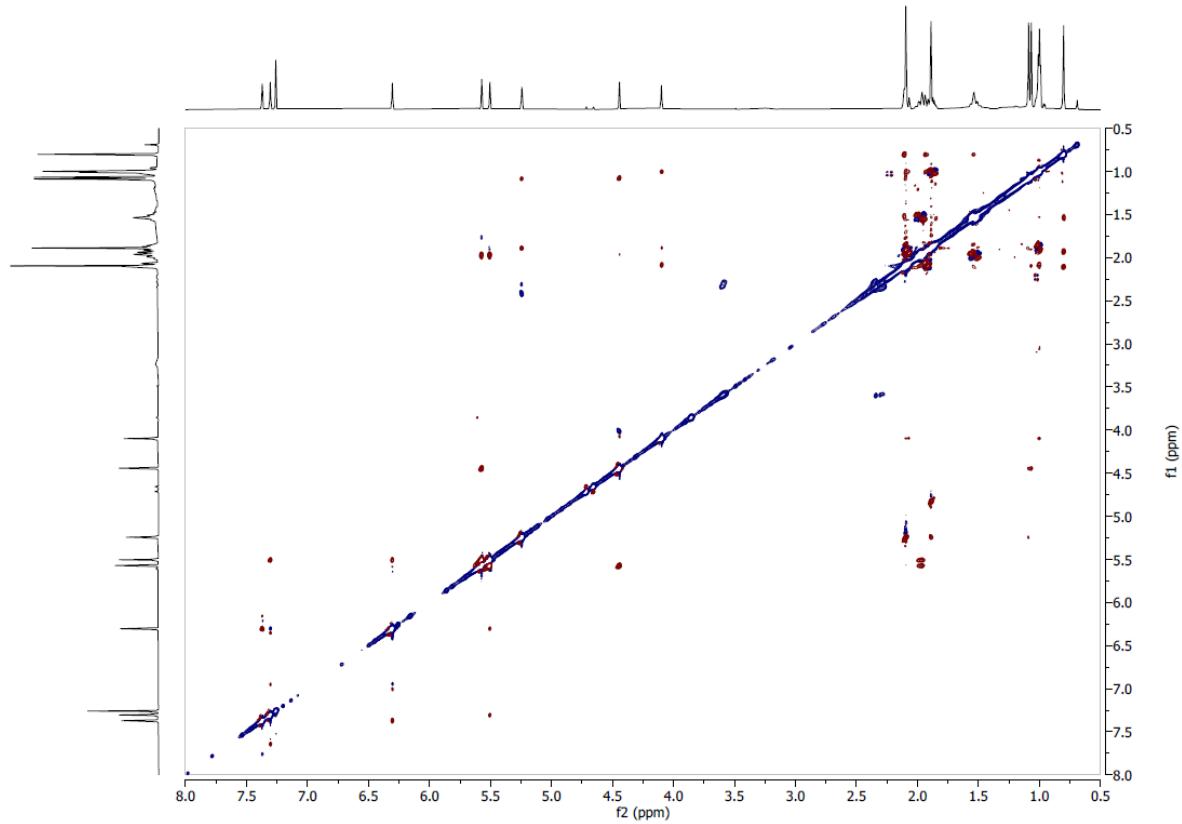
Supplementary Figure S4.2.191. ^{13}C -DEPTQ NMR spectrum of compound **33** in CDCl_3 at 151 MHz



Supplementary Figure S4.2.192. Edited HSQC NMR spectrum of compound **33** in CDCl_3

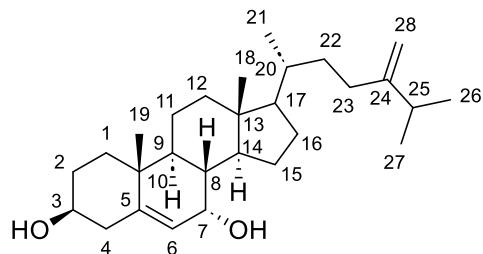


Supplementary Figure S4.2.193. HMBC NMR spectrum of compound 33 in CDCl_3

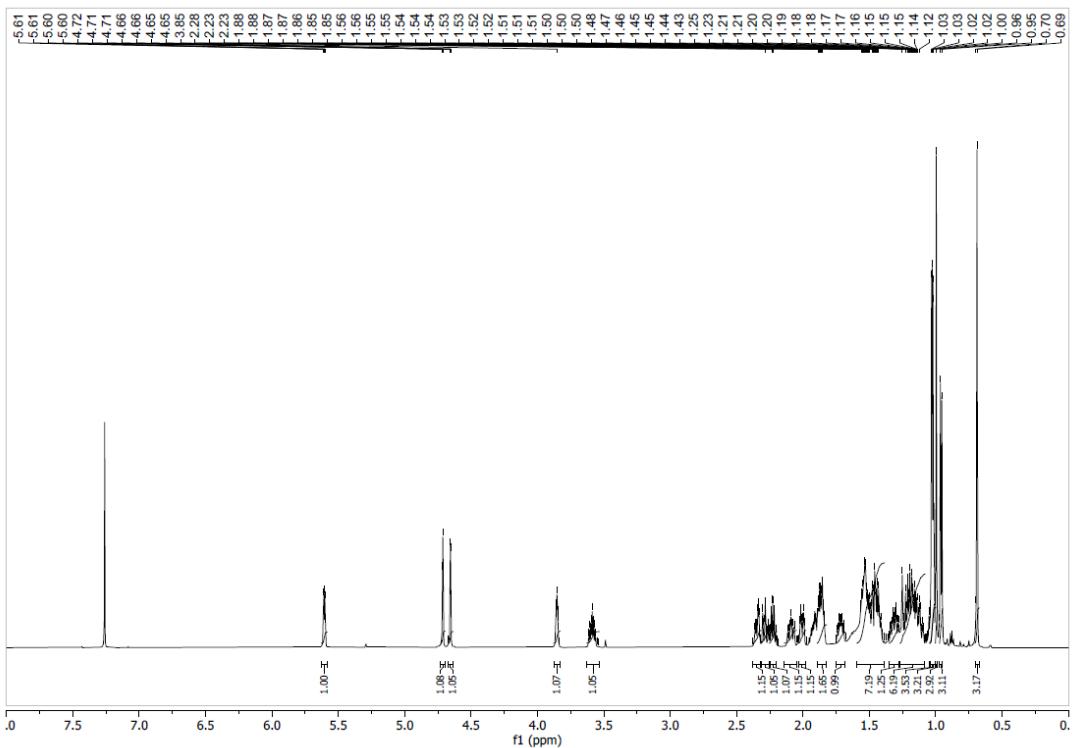


Supplementary Figure S4.2.194. ROESY NMR spectrum of compound 33 in CDCl_3

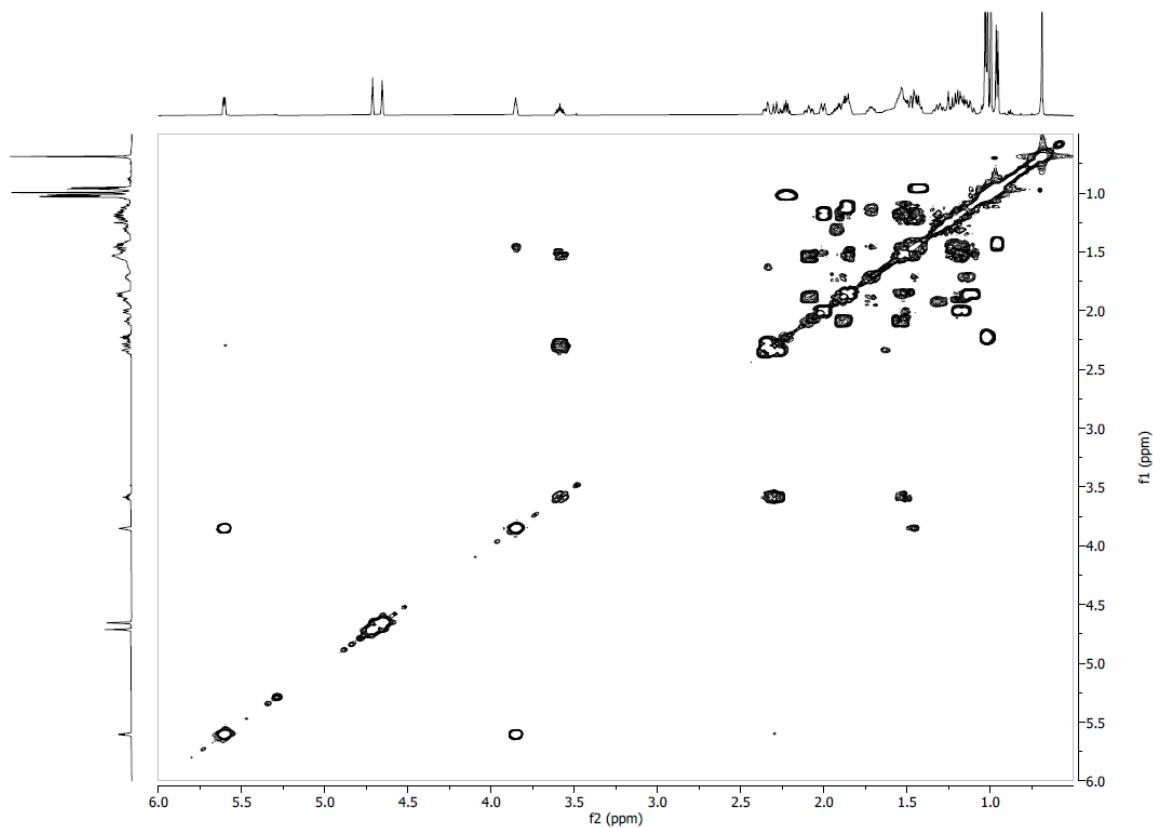
Compound **34**: 24-methylencholest-5-ene-3,7-diol [77]. Amorphous white powder, HRESIMS m/z 415.3559 [$M+H$]⁺ (calculated for C₂₇H₄₆O₂, error -2.64 ppm); $[\alpha]_D^{20}$ -6 (c 0.006 CHCl₃); UV (c 0.006, CHCl₃) λ_{max} 215, 241, 290.



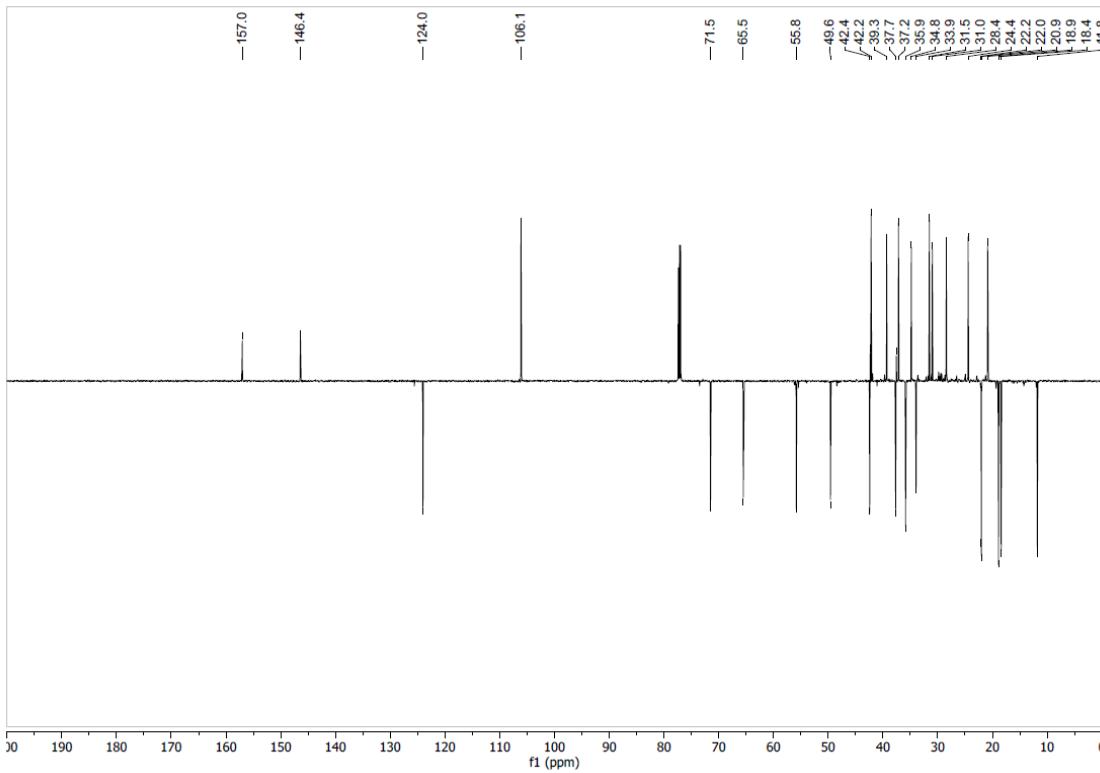
¹H NMR (CDCl₃, 600 MHz) δ 0.69 (3H, s, H₃-18), 0.96 (3H, d, J = 6.5 Hz, H₃-21), 1.00 (3H, s, H₃-19), 1.02 (3H, d, J = 6.8 Hz, H₃-27), 1.03 (3H, d, J = 6.8 Hz, H₃-26), 1.12 (1H, td, J = 14.2, 3.8 Hz, H-1a), 1.16 (1H, m, H-15¹¹), 1.17 (1H, m, H-12a), 1.18 (1H, m, H-22¹¹), 1.22 (1H, m, H-9), 1.31 (1H, m, H-16¹¹), 1.44 (1H, m, H-20), 1.45 (1H, m, H-14), 1.46 (1H, m, H-8), 1.48 (1H, m, H-11¹¹), 1.53 (2H, m, H-11', H-2b), 1.72 (1H, m, H-15'), 1.86 (2H, m, H-1b, H-2 α), 1.88 (1H, m, H-23¹¹), 1.92 (1H, m, H-16'), 2.01 (1H, dt, J = 12.7, 3.8 Hz, H-12 β), 2.09 (1H, ddd, J = 15.5, 11.3, 4.7 Hz, H-23'), 2.23 (1H, hept, J = 6.8 Hz, H-25), 2.28 (1H, tt, J = 13.2, 11.2, 1.9 Hz, H-4 α), 2.35 (1H, ddd, J = 13.2, 4.6, 1.9 Hz, H-4 β), 3.59 (1H, tt, J = 11.2, 4.6 Hz, H-3), 3.85 (1H, ddd, J = 5.4, 3.5, 1.7 Hz, H-7), 4.66 (1H, q, J = 1.5 Hz, H-28¹¹), 4.71 (1H, t, J = 1.5 Hz, H-28'), 5.61 (1H, dd, J = 5.4, 1.9 Hz, H-6); ¹³C NMR (CDCl₃, 151 MHz) δ 11.8 (CH₃-18), 18.4 (CH₃-19), 18.9 (CH₃-21), 20.9 (CH₂-11), 22.0 (CH₃-27), 22.2 (CH₃-26), 24.4 (CH₂-15), 28.4 (CH₂-16), 31.0 (CH₂-23), 31.5 (CH₂-2), 33.9 (CH-25), 34.8 (CH₂-22), 35.9 (CH-20), 37.2 (CH₂-1), 37.6 (C-10), 37.7 (CH-8), 39.3 (CH₂-12), 42.2 (CH₂-4), 42.3 (C-13), 42.4 (CH-9), 49.6 (CH-14), 55.8 (CH-17), 65.5 (CH-7), 71.5 (CH-3), 106.1 (CH₂-28), 124.0 (CH-6), 146.4 (C-5), 157.0 (C-24). Supplementary Figures S4.2.195-S4.2.200.



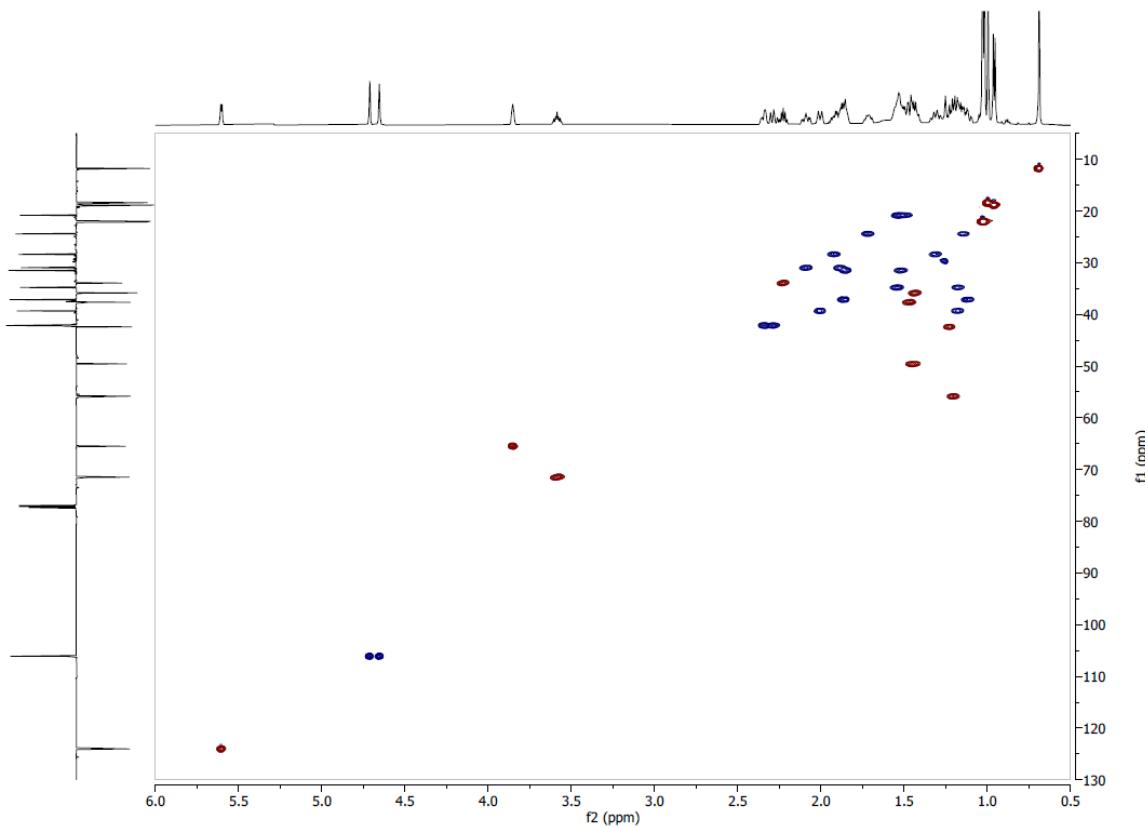
Supplementary Figure S4.2.195. ^1H NMR spectrum of compound **34** in CD_3OD at 600 MHz



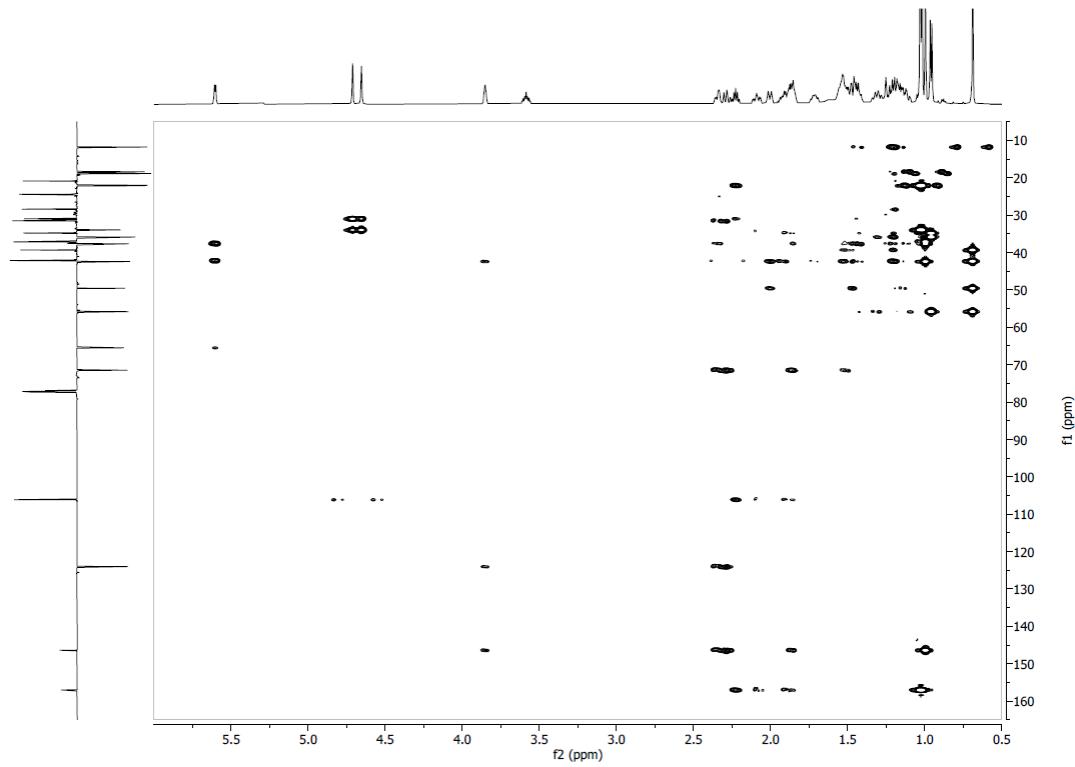
Supplementary Figure S4.2.196. COSY NMR spectrum of compound **34** in CD_3OD



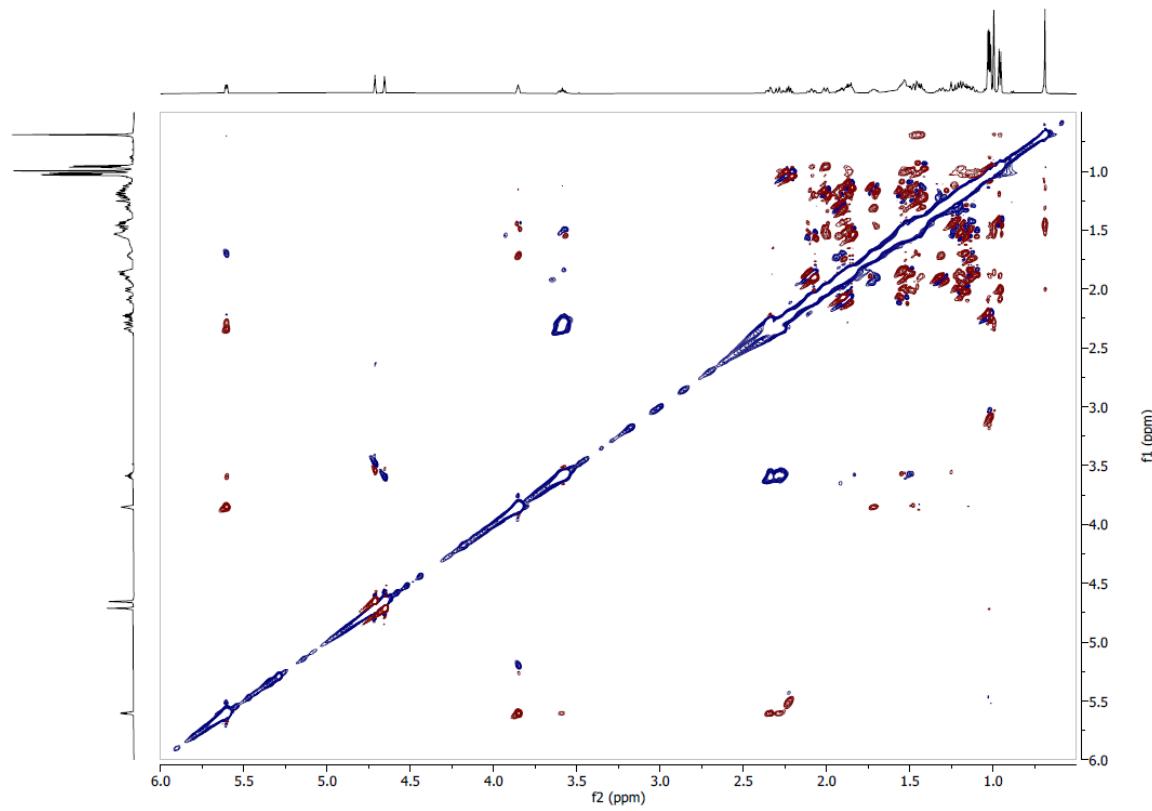
Supplementary Figure S4.2.197. ^{13}C -DEPTQ NMR spectrum of compound **34** in CD_3OD at 151 MHz



Supplementary Figure S4.2.198. Edited HSQC NMR spectrum of compound **34** in CD_3OD



Supplementary Figure S4.2.199. HMBC NMR spectrum of compound **34** in CD_3OD



Supplementary Figure S4.2.200. ROESY NMR spectrum of compound **34** in CD_3OD