

**Reactivity of alicyclic 1,5,9-triketones toward five-, six-, and seven-membered rings in acidic medium.
Stereochemistry of intramolecular cyclization products**

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Supporting Information

9-Oxapentacyclo[15.3.1.0^{1,10}.0^{3,8}.0^{10,15}]heneicosan-3(8)-en-21-one (15). Yield 0.39 g (81%), colorless needles, mp 116–118°C (EtOH). ¹H NMR spectrum, δ , ppm: 1.17–1.73 (15H, m) and 1.75–2.14 (11H, m, 13CH₂); 2.28–2.38 (1H, m, 15-CH); 2.40–2.47 (1H, m, 17-CH). ¹³C NMR spectrum, δ , ppm: 21.1; 21.7; 23.1; 23.2; 26.1; 27.0; 27.4; 27.9; 28.1; 32.1 (C-1); 35.6; 36.5; 38.0; 39.8 (C-15); 46.5 (C-17); 51.9 (C-1); 82.2 (C-10); 103.9 (C-3); 142.7 (C-8); 217.3 (C-21).

(1S*,10S*,15S*,17S*)-9-Oxapentacyclo[15.2.1.0^{1,10}.0^{3,8}.0^{10,15}]eicos-3(8)-en-20-one (16a). Yield 0.65 g (65%), colorless needles, mp 84–85°C (EtOH). GC/MS *t*_r 9.88. IR spectrum, ν , cm⁻¹: 1694 (dihydropyridine cycle), 1746 (C=O). ¹H NMR spectrum, δ , ppm: 1.10–1.21 (1H, m, CH₂); 1.22–1.50 (6H, m, CH₂); 1.52–2.10 (17H, m, CH₂); 1.81–1.91 (1H, m, 15-CH); 2.24–2.32 (1H, m, 17-CH). ¹³C NMR spectrum, δ , ppm: 21.0; 21.6; 23.2; 23.3; 25.9; 26.2; 26.4; 27.1 (C-2); 27.4; 28.4 (2C); 37.6 (C-16); 37.4 (C-15); 44.2 (C-17); 50.6 (C-1); 83.0 (C-10); 104.6 (C-3); 143.8 (C-8); 216.1 (C-20). Mass spectrum, *m/z* (*I*_{rel.}, %): 286 [M]⁺ (100), 188 (17), 149 (42), 91 (25), 55 (13). Found, %: C 79.60; H 8.96. C₁₉H₂₆O₂. Calculated, %: C 79.68; H 9.15.

(1S*,10R*,15S*,17S*)-9-Oxapentacyclo[15.2.1.0^{1,10}.0^{3,8}.0^{10,15}]eicos-3(8)-en-20-one (16b). Yield 0.30 g (67%), colorless needles, mp 144–145°C. GC/MS *t*_r 10.18. IR spectrum, ν , cm⁻¹: 1694 (dihydropyridine cycle), 1746 (C=O). ¹H NMR spectrum, δ , ppm (*J*, Hz): 0.86–0.99 (1H, m, CH₂); 1.09–1.76 (12H, m, CH₂); 1.15 (1H, d, *J* = 17.1, 2-CH₂); 1.55 1.51–1.59 (1H, m, CH₂); 1.78–2.07 (6H, m, CH₂); 1.89–1.99 (1H, m, 16-CH₂); 2.12–2.31 (2H, m, CH₂); 2.34–2.41 (1H, m, 17-CH); 2.46 (1H, d, *J* = 17.1, 2-CH₂). ¹³C NMR spectrum, δ , ppm: 20.6; 21.9; 22.0; 23.2; 23.4; 24.5; 25.6; 27.4; 28.1; 28.5 (C-2); 28.7; 34.2 (C-15); 34.4 (C-16); 45.1 (C-17); 50.6 (C-1); 79.9 (C-10); 102.3 (C-3); 142.9 (C-8); 218.0 (C-20). Mass spectrum, *m/z* (*I*_{rel.}, %): 286 [M]⁺ (46), 191 (18), 149 (100), 136 (21), 91 (17). Found, %: C 79.65; H 8.98. C₁₉H₂₆O₂. Calculated, %: C 79.68; H 9.15.

9-Oxapentacyclo [15.4.1.0^{1,10}.0^{3,8}.0^{10,15}]docos-3(8)-en-22-one (17). Yield 0.30 g (70%), colorless needles, mp 153–154°C (EtOH), GC/MS *t*_r 11.12. IR spectrum, ν , cm⁻¹: 1694 (dihydropyridine cycle), 1746 (C=O). ¹H NMR spectrum, δ , ppm (*J*, Hz): 1.10–1.31 (4H, m, CH₂); 1.33–2.09 (20H, m, CH₂); 1.44 (1H, dd, *J* = 13.0, *J* = 5.0, 16-CH₂); 1.52 (1H, d, *J* = 16.0, 2-CH₂); 2.03 (1H, td, *J* = 13.0, *J* = 7.6, 16-CH₂); 2.11–2.21 (1H, m, 15-CH); 2.54 (1H, d, *J* = 16.0, 2-CH₂); 2.65–2.73 (1H, m, 17-CH). ¹³C NMR spectrum, δ , ppm: 21.2; 23.1; 23.3; 25.5; 25.6; 25.9; 26.9; 27.2; 28.1; 29.1; 33.8 (C-2); 33.9; 34.4; 34.6 (C-16); 35.8 (C-15); 47.5 (C-17); 53.5 (C-1); 80.2 (C-10); 104.4 (C-3); 142.9 (C-8); 213.7 (C-22). Mass spectrum, *m/z* (*I*_{rel.}, %): 314 [M]⁺ (56), 271 (15), 204 (100), 161 (22), 147 (20), 91 (18). Found, %: C 80.12; H 9.46. C₂₁H₃₀O₂. Calculated, %: C 80.21; H 9.62.

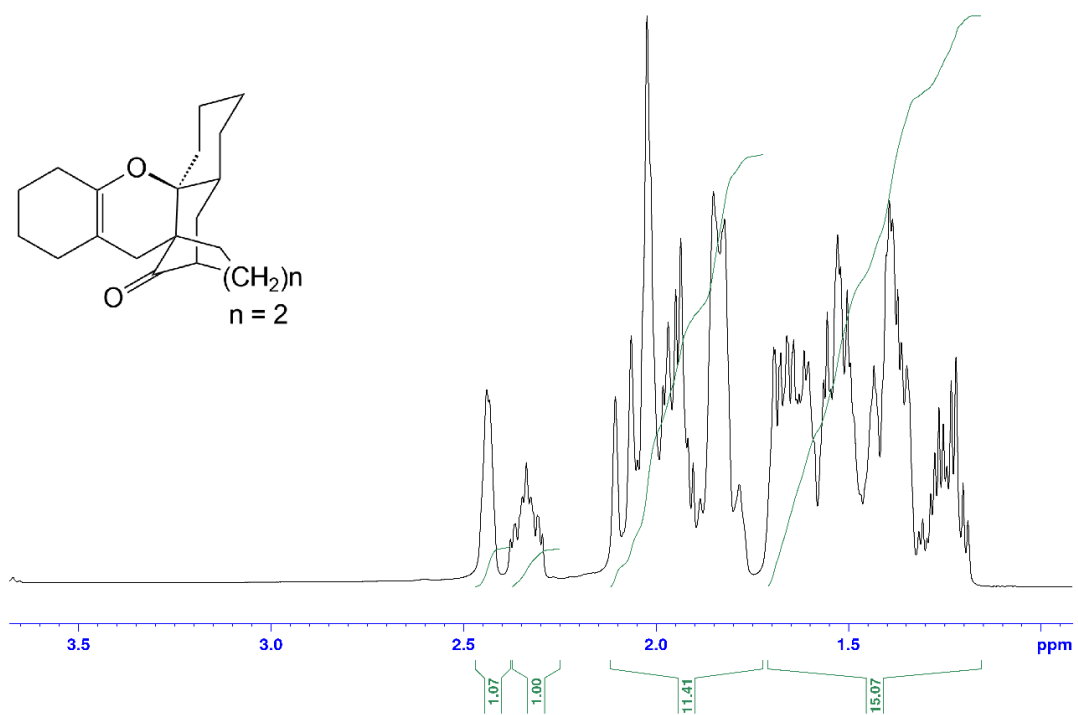


Figure S1. ¹H NMR spectrum of 9-Oxapentacyclo[15.3.1.0^{1,10}.0^{3,8}.0^{10,15}]heneicosan-3(8)-en-21-one (15)

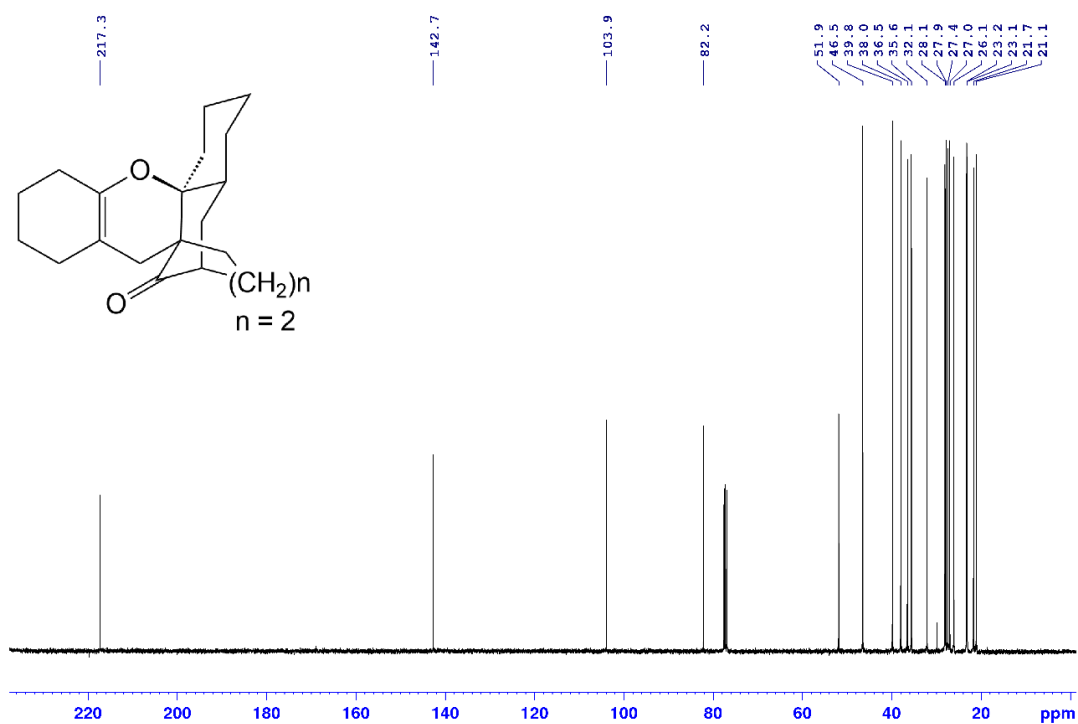


Figure S2. ¹³C NMR spectrum of 9-Oxapentacyclo[15.3.1.0^{1,10}.0^{3,8}.0^{10,15}]heneicosan-3(8)-en-21-one (15).

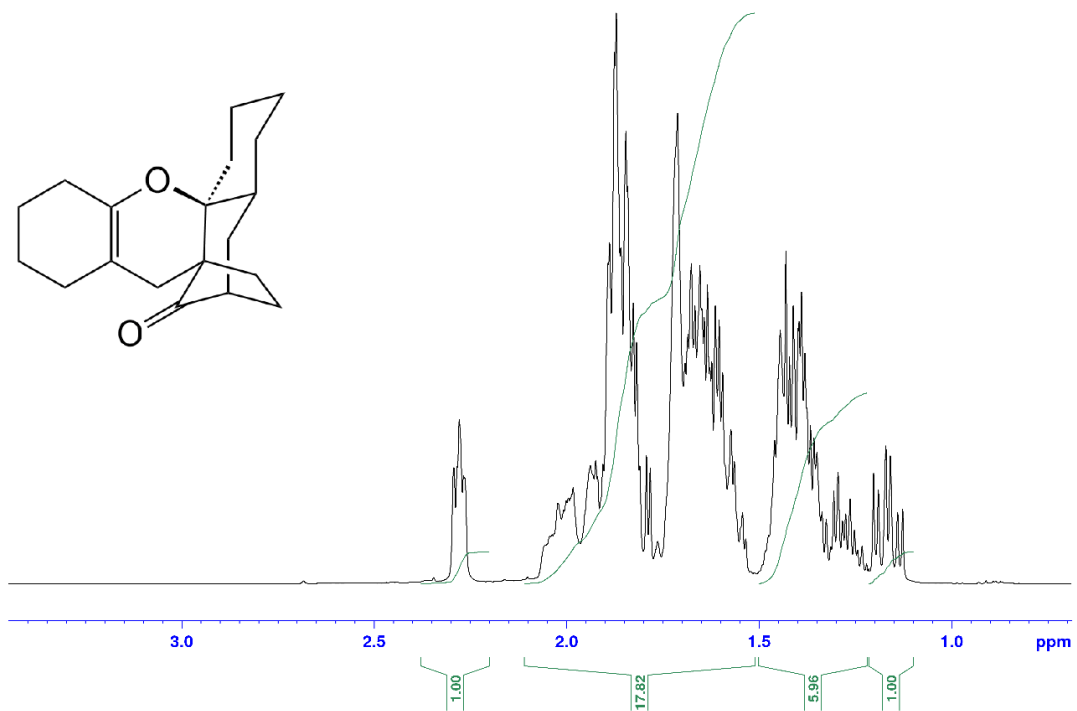


Figure S3. ^1H NMR spectrum of (1*S**,10*S**,15*S**,17*S**)-9-Oxapentacyclo[15.2.1.0^{1,10}.0^{3,8}.0^{10,15}]eicos-3(8)-en-20-one (16a)

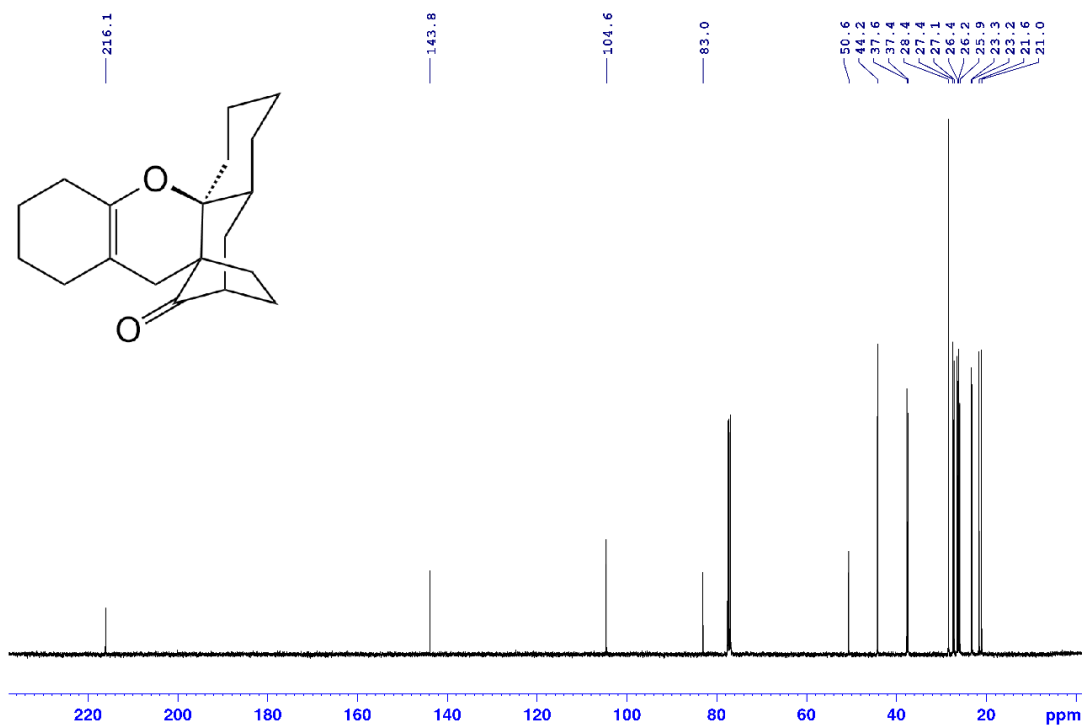


Figure S4. ^{13}C NMR spectrum of (1*S**,10*S**,15*S**,17*S**)-9-Oxapentacyclo[15.2.1.0^{1,10}.0^{3,8}.0^{10,15}]eicos-3(8)-en-20-one (16a)

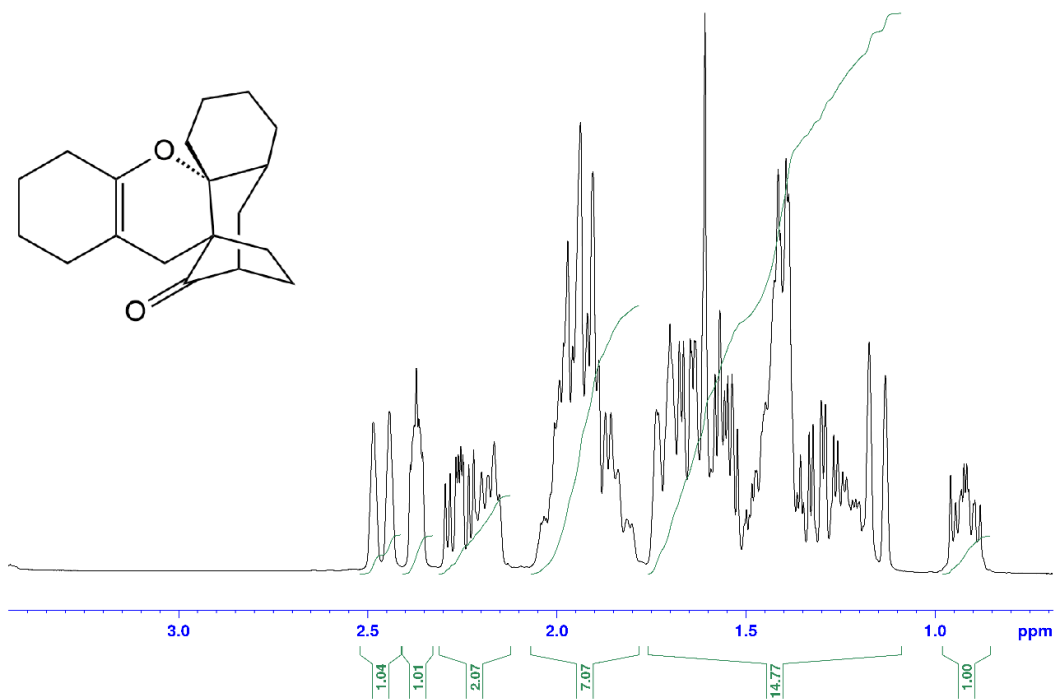


Figure S5. ^1H NMR spectrum of (1*S**,10*R**,15*S**,17*S**)-9-Oxapentacyclo[15.2.1.0^{1,10}.0^{3,8}.0^{10,15}]jeicos-3(8)-en-20-one (16b)

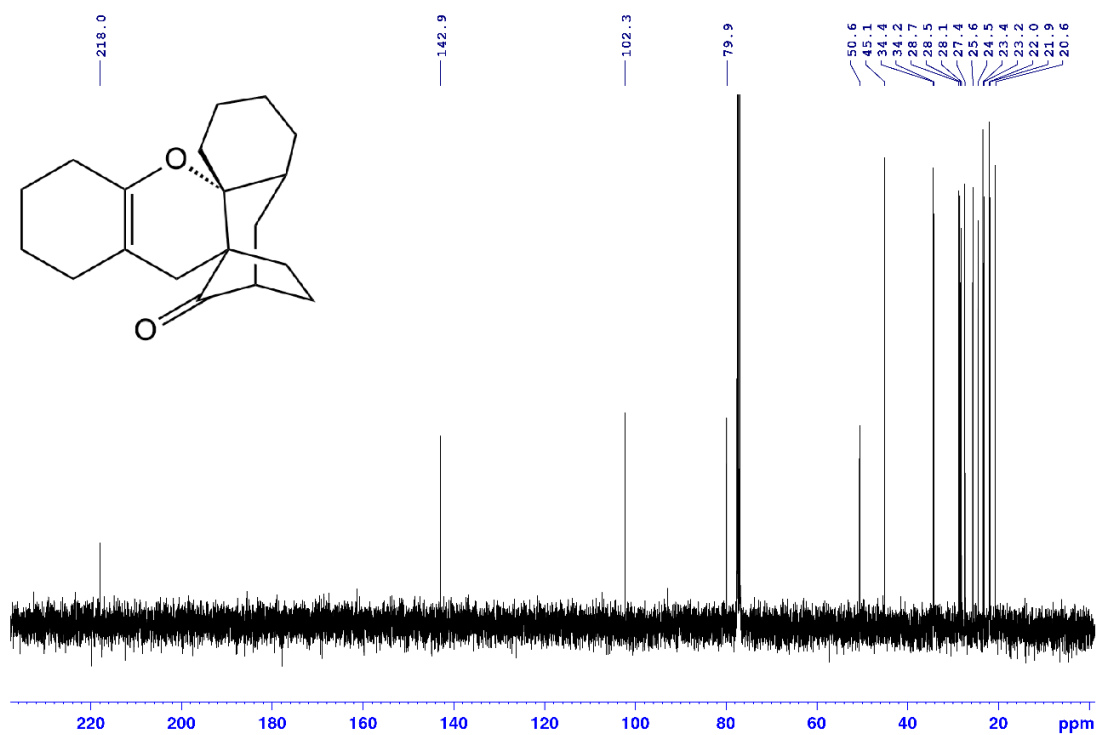


Figure S6. ^{13}C NMR spectrum of (1*S**,10*R**,15*S**,17*S**)-9-Oxapentacyclo[15.2.1.0^{1,10}.0^{3,8}.0^{10,15}]jeicos-3(8)-en-20-one (16b)

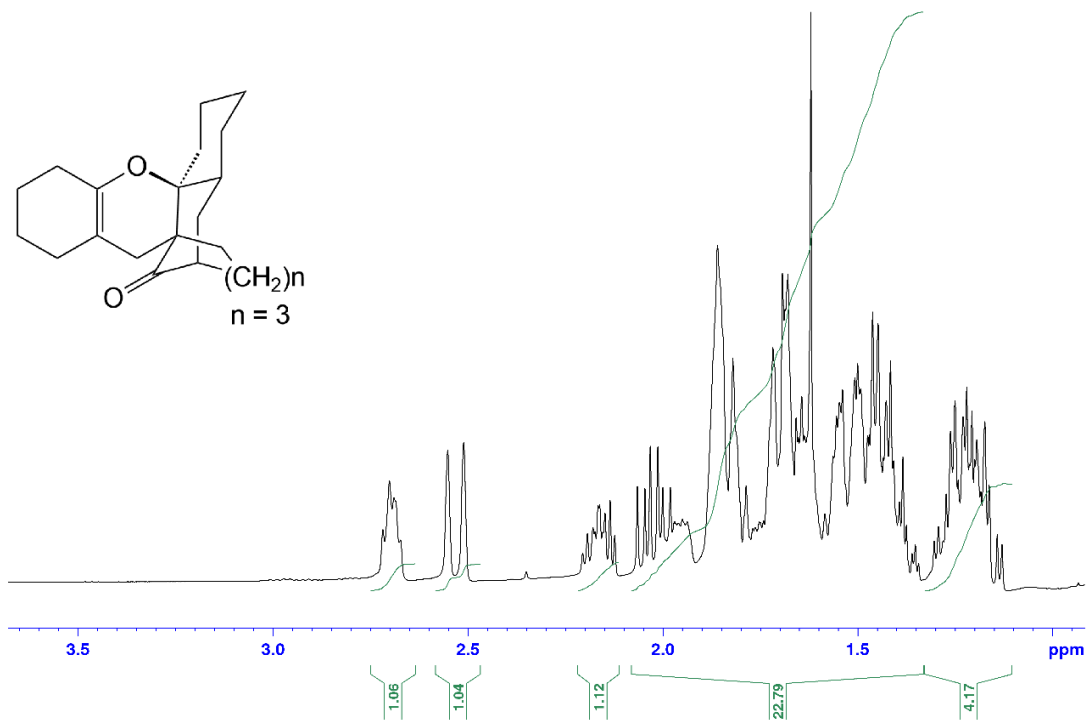


Figure S7. ¹H NMR spectrum of 9-Oxapentacyclo [15.4.1.0^{1,10}.0^{3,8}.0^{10,15}]docos-3(8)-en-22-one (17)

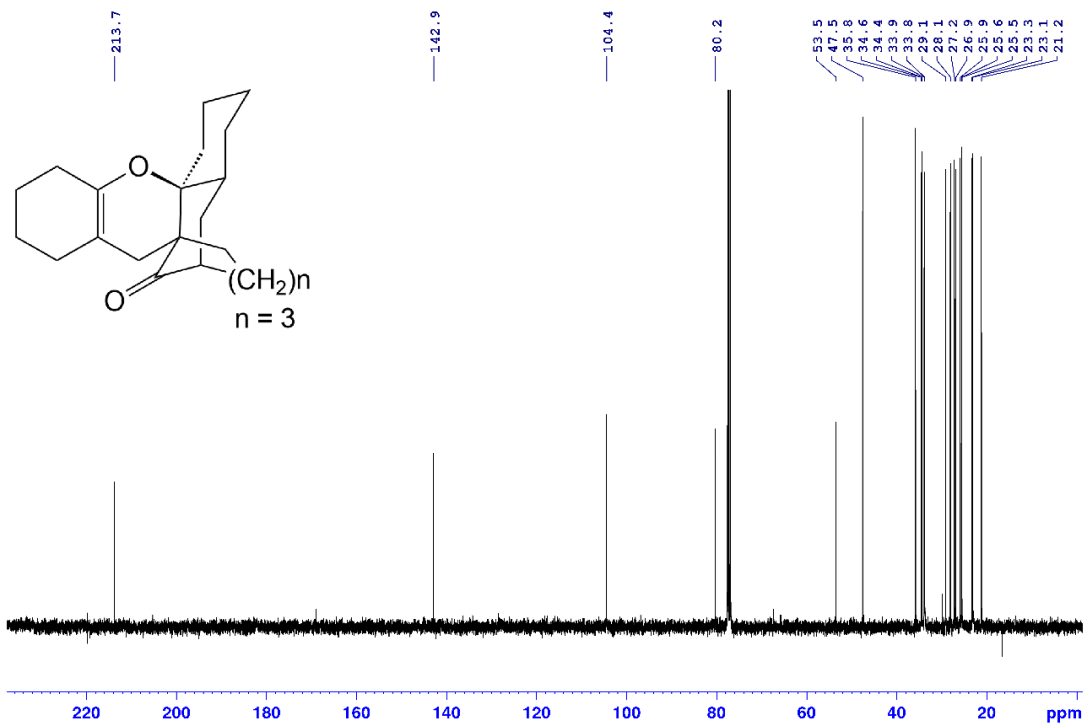


Figure S8. ¹³C NMR spectrum of 9-Oxapentacyclo [15.4.1.0^{1,10}.0^{3,8}.0^{10,15}]docos-3(8)-en-22-one (17)