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Supplementary Material

Spectroscopic and Analytical Data

General

The ^1H (300 MHz) and ^{13}C (75.5 MHz) NMR spectra were recorded on a General Electric QE-300 instrument and are referenced to tetramethylsilane. Elemental analyses were performed at Oneida Research Services, Inc., Whitesboro, NY.

Anti-cis-2,3-Isopropylidenedioxy-5-p-toluenesulfonylbicyclo[2.2.2]octa-5,8-diene

^1H NMR (CDCl_3): δ 7.67 (d, 2H), 7.29 (d, 2H), 7.12 (d of d, 1H), 6.24 (t, 1H), 6.17 (t, 1H), 4.22 (d of d, 1H), 4.09 (d of d, 1H), 4.08 (m, 1H), 3.99 (m, 1H), 2.41 (s, 3H), 1.25 (s, 3H), 1.18 (s, 3H). ^{13}C NMR (CDCl_3): δ 147.5, 144.6, 142.0, 135.6, 131.3, 131.1, 129.9, 127.9, 113.6, 78.5, 78.1, 43.6, 42.1, 25.7, 25.5, 21.6.

Analysis: Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_4\text{S}$: C, 65.04; H, 6.06. Found: C, 65.05; H, 6.02.

Cis-2,3-Isopropylidenedioxybicyclo[2.2.2]octa-5,8-diene

^1H NMR (CDCl_3): δ 6.28 (d of d, 2H), 6.23 (d of d, 2H), 4.13 (s, 2H), 3.80 (br s, 2H), 1.30 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (CDCl_3): δ 133.7, 132.0, 112.6, 78.5, 42.0, 26.0, 25.5.

Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_2$: C, 74.13; H, 7.42. Found: C, 74.44; H, 7.89.

Bicyclo[2.2.2]octa-5,8-diene-cis-2,3-diol

^1H NMR (CDCl_3): δ 6.36 (t, 2H), 6.20 (d of d, 2H), 3.77 (d, 2H), 3.65 (t, 2H), 2.80 (d of t, 2H). ^{13}C NMR (CDCl_3): δ 133.0, 132.5, 67.3, 44.4.

Anal. Calcd for $\text{C}_8\text{H}_{10}\text{O}_2$: C, 69.55; H, 7.29. Found: C, 69.53; H, 7.10.

Bicyclo[2.2.2]octa-5,8-diene-cis-2,3-diol diacetate

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¹H NMR (CDCl₃): δ 6.41 (d of d, 2H), 6.31 (d of d, 2H), 4.79 (s, 2H), 3.78 (br s, 2H), 1.97 (s, 6H). ¹³C NMR (CDCl₃): δ 170.3, 133.6, 132.5, 69.1, 41.2, 20.8.

Anal. Calcd for C₁₂H₁₄O₄: C, 64.85; H, 6.35. Found: C, 64.89; H, 6.32.

Bicyclo[2.2.2]octa-5,8-diene-cis-2,3-diol bis(methylcarbonate)

¹H NMR (CDCl₃): δ 6.43 (d of d, 2H), 6.33 (d of d, 2H), 4.72 (s, 2H), 3.87 (m, 2H), 3.71 (s, 6H). ¹³C NMR (CDCl₃): δ 155.3, 133.4, 132.2, 72.0, 54.8, 41.1.

Anal. Calcd for C₁₂H₁₄O₆: C, 56.69; H, 5.55. Found: C, 56.88; H, 5.60.