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Synthesis of a Tight Intramolecular OH···Olefin Interaction, Probed by IR, ^{1}H NMR, and Quantum Chemistry

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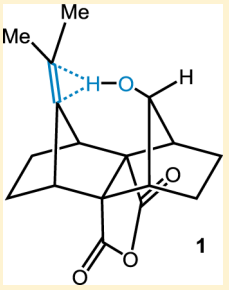
Supporting Information

ABSTRACT: We have synthesized a molecule containing a tight hydrogen-bonding interaction between an alcohol and a nonconjugated π-system. The strength of this hydrogen bond results in a large red shift, nearly 189 cm^{-1}, on the alcohol stretching frequency in the IR spectrum in comparison to a free alcohol control. The interaction is notable in that it possesses a better defined intramolecular hydrogen bond compared to the usual molecules for which it is noted, such as *syn*-7-norbornenol. This interaction was studied through the use of IR and NMR spectroscopy, X-ray crystallography, and molecular modeling calculations.



Hydrogen bonds play a huge role in how the world works, from imparting unique properties to water to controlling the genetic code. Since they were first determined to be a viable chemical interaction, the effects of hydrogen bonding have been the subject of countless studies. Over the years, a perfect definition of a hydrogen bond has remained elusive; one of the first was put forth by Pauling, who classified them as electrostatic **A**–H···**B** interactions wherein both **A** and **B** are electronegative atoms.[1] Later, this was expanded upon by Pimentel and McClellan to consist of **A**–H···**B** interactions wherein there is direct evidence of bond formation in which the hydrogen on **A** plays a key role.[2] This greatly expanded the definition of H-bonding, for now many weak or "nonclassical" H-bonds could be included. However, the openness of the definition is a mixed blessing, as the sheer number of hydrogen-bonding-like interactions makes it difficult to nail down exact criteria for their formation. In addition to the classic OH···O interactions, such as in water, other classical and nonclassical (weak) interactions have been intensely studied over the past decades, such as OH···F,[3] NH···N,[4] FH···F,[5] and CH···π.[6] While a fair number of studies have investigated the more popular H-bonding interactions to aromatic π-systems such as pyridine,[7] arenes,[8] and indoles,[9] there are relatively few published studies concerning nonconjugated double bonds. Even so, OH···π interactions (Figure 1) have been identified as assisting in a few biological pathways, like in the binding of the disaccharide trehalose.[10] In this paper, we report the synthesis and study of a cage system, **1**, that displays a close interaction between an OH group and a tetrasubstituted double bond. Spectroscopic and crystallographic evidence indicates a significant interaction that more closely mimics the orientation of a calculated optimal intermolecular interaction (**2**).

Of the few studies that have been published on OH···π interactions in nonconjugated π-systems, all have documented fairly weak H-bonding interactions. The majority of cases have

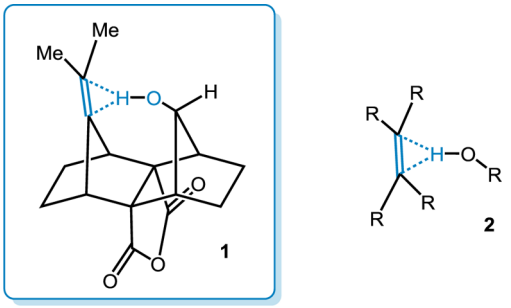


Figure 1. Intra- and intermolecular OH···π interactions.

the alcohol group positioned too far away or situated poorly for the interaction from a geometric standpoint.[11] Some well-studied examples of weak OH···π interactions can be observed in 3-buten-1-ol[12] and *o*-allylphenol.[13,14] However, due to the large degree of rotational freedom present in these molecules, the majority of them exist in an unbound state in solution. Several other studies have been undertaken to characterize the OH···π system in *syn*-7-norbornenol due to its conveniently placed alcohol group and relative lack of rotational freedom.[15,16] With its alcohol group positioned in close proximity to the double bond, a clear preference for the OH···π interaction is seen in the IR spectrum, an observation that is backed up by molecular modeling calculations. In addition, the molecule has an ideal control in its epimer *anti*-7-norbornenol, wherein the hydroxyl group is pointed away from the double bond. Previous studies, both experimental and theoretical, have confirmed the existence of a hydrogen bond, represented by a notable red shift in the IR spectrum (57 cm^{-1}) in comparison to *anti*-7-norbornenol in CCl_4.[17] However, due to the poor positioning of the alcohol in

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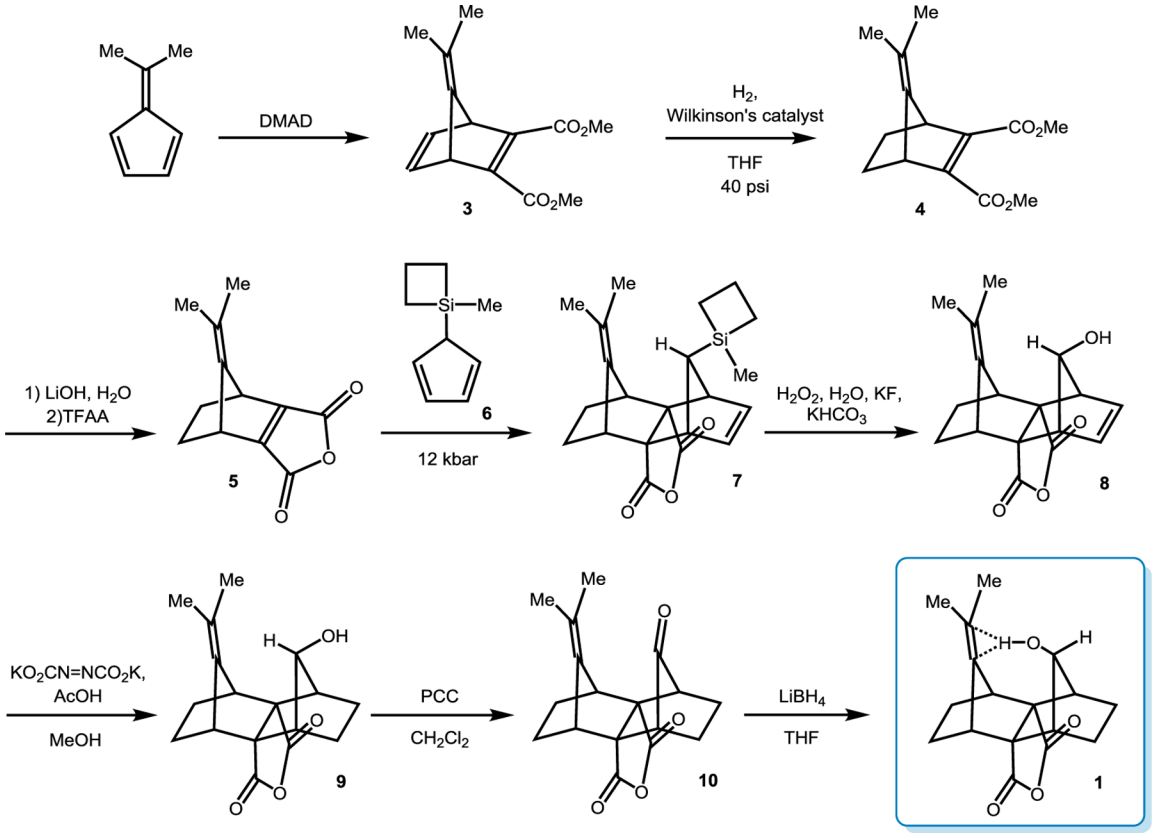

Figure 2. Synthetic pathway for the generation of **1**.

syn-7-norbornenol, which is at an awkward angle and a fair distance away, the interaction is still non-optimal (the dihedral angle between the O−H bond and the C═C double bond (H−O···C(2)═C(3)) is about 81° at the ωB97XD/cc-pVTZ level of theory). What is more, the interaction is characterized by the presence of no bond critical point (BCP) at suitable levels of theory. While this measure of the existence of hydrogen bonds is (in some cases, hotly) debatable, it does, in a certain way, represent H-bonding strength.[18] Ideally, a strong ROH···C═C interaction should have a dihedral angle of 0°, resulting in the O−H bond and the C═C double bond lying in the same plane. Previously, our lab has published studies that utilized a sesquinorbornane scaffold to hold functional groups in close proximity to investigate intramolecular interactions, such as anchimeric assistance by fluorine,[19] F···H interactions,[20] a close fluorine olefin interaction,[21] and a strong OH···F interaction.[3] Building on our previous work, we knew using a similar molecular scaffold as the latter would bring the OH group and the double bond into close contact as well as place them nearly orthogonally, perfect for hydrogen-bonding overlap. In addition, the double bond could be tetrasubstituted with electron-donating aliphatic groups. The sum of all these factors should result in a more intense hydrogen-bonding interaction.

We began our investigation of this putative tight OH···π bond by probing the interaction through molecular modeling calculations. The vibrational modes for both the *in*- and *out*-alcohols were predicted using the ωB97XD/cc-pVTZ basis set, due to its reputation for accurately predicting dispersion effects.[22] The calculated OH shifts place the *in*-OH of **1** red-shifted, compared to the *out*-OH of **9**, with a difference of 167 cm^{-1}. This is an impressive (albeit predicted) red shift, over twice the difference between the *syn*- and *anti*-epimers of 7-norbornenol.[17] The calculation also places the alcohol hydrogen of the *in*-OH of **1** only 1.974 and 2.076 Å from the olefin's bond ends, compared to the predicted 2.540 and 2.541 Å in *syn*-7-norbornenol, with the same method and basis set. To double check the accuracy of the method, the *anti*/*syn*-7-norbornenol red shift was calculated and found to be 67 cm^{-1} at the same level of theory. Another test was to compare the energy calculation of **1** to a non-hydrogen-bound version of **1** where the OH bond is rotated 180°. The results predict **1** to be 7.30 kcal more stable than the non-hydrogen-bound version. Additionally, electron density (ρ) calculations using the quantum theory of atoms in molecules (AIM) program indicate a BCP between the alcohol hydrogen and the olefin, ρ = 0.036.[23]

For a better understanding of the strength of the interactions, intramolecular hydrogen bonds are often compared to analogous intermolecular hydrogen-bonding interactions. From a computational standpoint, one control interaction is the intermolecular H-bond of methanol and ethylene.[24] This interaction and the related system of water and ethylene have been the topic of multiple computational studies.[25] However, we believe a model that is a better match for our cage molecule would be the complex of tetramethylethylene and MeOH (**2**, R = Me). This would take into account the electron-donating capabilities of the methyl and aliphatic groups substituted on the double bond of **1** (Figure 2). For our investigation, the interaction of tetramethylethylene and MeOH was optimized using the same method and basis set as the previous calculations (ωB97XD/cc-pVTZ). The predicted distances to the sp^2 carbons, 2.279 and 2.315 Å, are somewhat looser than those predicted for **1**. The predicted red shift for the control was 39 cm^{-1}.

In order to integrate the olefin into our sesquinorbornane scaffold, a new dienophile (**5**) was designed for the synthesis.

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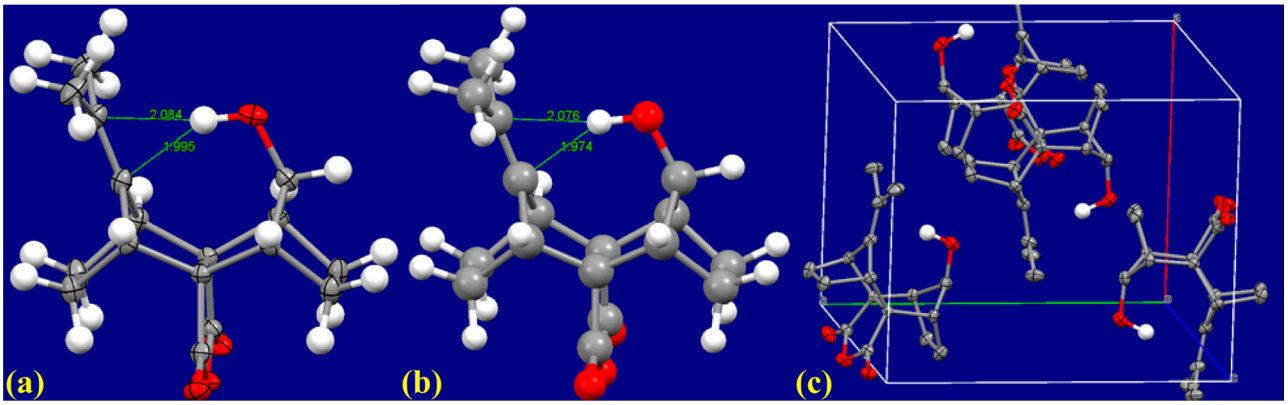

Figure 3. (a) Crystal structure of **1** determined from single-crystal X-ray diffraction (displacement ellipsoids given at 50% probability level). The O−H bond distance was restrained to the value calculated in the density functional theory equilibrium calculation (0.963 Å). (b) Equilibrium structure calculation of **1** at ωB97XD/cc-pVTZ. (c) Crystal packing diagram of **1**. Except for the alcohol hydrogen, all hydrogen atoms have been removed for ease of observation.

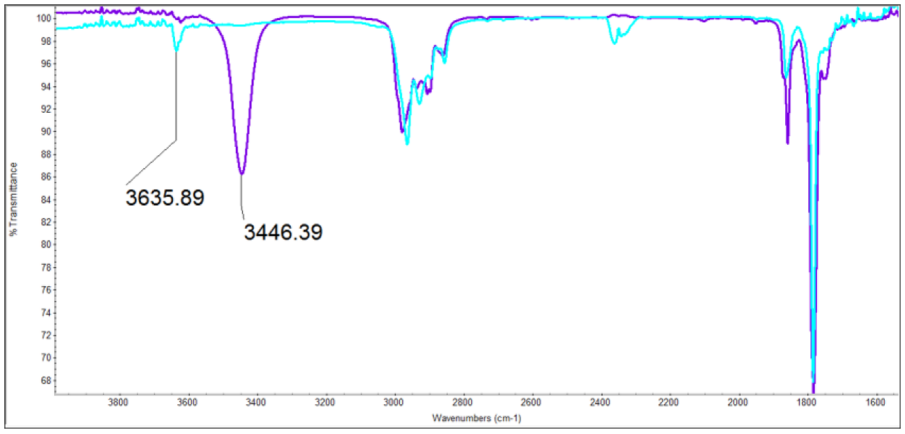

Figure 4. Overlay of the IR spectra of **1** (purple) and **9** (blue), in carbon tetrachloride, highlighting the large red shift in the alcohol stretching frequency.

The route begins with 6,6-dimethylfulvene, which was allowed to react neatly with dimethylacetylene dicarboxylate (DMAD) to yield the trienediester **3**. Wilkinson's catalyst was employed to reduce the least substituted double bond, yielding **4**. This reduction was followed by saponification of the carbomethoxy groups with LiOH to form a dicarboxylic acid, which was then converted without workup into the corresponding anhydride using trifluoroacetic anhydride (TFAA). With this new dienophile in hand, it was treated with **6** at high pressure to perform the Diels−Alder reaction that makes the sesquinorbornane scaffold **7**. This was followed by a Fleming-Tamao oxidation to convert the silane to alcohol **8** and a diimide reduction to reduce selectively the less substituted double bond. Similar to the *anti*/*syn*-7-norbornenol system, this *out*-alcohol (**9**) serves as an ideal control to study the strength of the H-bonding interaction. Alcohol **9** was oxidized to a ketone (**10**) by treatment with pyridinium chlorochromate (PCC) and then reduced stereospecifically with $LiBH_4$ to form **1**.

A single crystal of **1** was obtained through solvent evaporation from a solution in dichloromethane, and crystallographic measurements were performed using X-ray diffraction. The framework crystallographic analysis with the alcohol O−H bond restrained to 0.963(7) Å shows a very close OH···π interaction (predicted distances to the sp^2 carbons: 1.995 and 2.084 Å), which is in agreement to the predicted distances of 1.974 and 2.076 Å at the ωB97XD/cc-pVTZ level of theory, as shown in Figure 3. No signs of bifurcation of the OH bond were noted in the crystal packing.

A survey of the Cambridge Structural Database (CSD)[26] was carried out to identify molecules with similar interactions. The search criteria were alcohols coordinated to double bonds (OH···C(sp^2) distances constrained to 1.8−2.2 Å). Only one molecule (CSD refcode: JOCQEX), a pentaol that is an intermediate in a paclitaxel synthesis, was found to contain a serendipitous interaction that was within the criteria.[27] The crystal structure records the distances from the alcohol hydrogen to the sp^2 carbons as 1.994(16) and 2.080(8) Å. However, upon investigation of the packing diagram, there appears to be some bifurcation in the OH bond. In addition, a comparative red shift for the putative hydrogen-bonding interaction is hard to estimate as only minimal IR data are reported and the molecule contains five hydroxyl groups.

IR studies of **1** and **9** corroborate the molecular modeling predictions. When the two OH stretches were compared, it was immediately clear the bound alcohol of **1** has a far more intense OH stretch than the free alcohol of **9**. Also, the actual red shift in the IR spectrum was, in fact, greater than the prediction, measuring 188 cm^{-1}. These measurements were performed on dilute (10^{-2} M) samples in dichloromethane. When the solvent was changed to carbon tetrachloride, the interaction was unaffected as **1** was observed to have a red shift of 189 cm^{-1}

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compared to **9** (see Figure 4). Such a large red shift would seem to indicate a substantial interaction.

In the ^{1}H NMR, the alcohol hydrogen of **1** is found at 4.05 ppm, likely due to the deshielding effects of the C═C bond. Another example of this trend was observed in the proton geminal to the alcohol. In **1**, the geminal proton, 4.26 ppm, is pointed away from the olefin and effectively free from the influence of the C═C bond. However, in **9**, the geminal proton is noticeably deshielded, compared to **1**, at 5.27 ppm. Another indication of how tight the hydrogen is held is the lack of exchange with the deuterated chloroform contaminated with traces of DCl. The integrations of the alcohol peak reveal that only a negligible amount of the proton in **1** exchanged, whereas the OH protons of **9** exchanged rapidly and completely.

In conclusion, our results show that **1** does indeed contain a tight hydrogen-bonding interaction between the alcohol and the nonconjugated π-system. This is most evident in the IR spectrum, where **1** is red-shifted 188−189 cm^{-1} from the control system **9** and is shown to contain no unbound alcohol. In addition, our molecular modeling calculations show that **1** positions the alcohol far closer to the double bond compared to previously studied systems. This is a notable change when compared to the previous molecules studied, such as *syn*-7-norbornenol, whose bond distances were not very different from the free methanol/tetramethylethylene system. With the evidence from both molecular modeling and experimental measurements, it is clear that our system possesses a more significant hydrogen-bonding interaction than previously seen and thus is a more revealing probe of this phenomenon.

EXPERIMENTAL SECTION

General Methods. Unless otherwise stated, all reactions were carried out under strictly anhydrous, air-free conditions under nitrogen. All solvents and reagents were dried and distilled by standard methods. ^{1}H and ^{13}C spectra were acquired on a 400 MHz NMR in $CDCl_3$ at 25 °C. The ^{1}H and ^{13}C chemical shifts are given in parts per million (δ) with respect to an internal tetramethylsilane (TMS, δ 0.00 ppm) standard. NMR data are reported in the following format: chemical shifts (multiplicity (s = singlet, d = doublet, t = triplet, q = quartet m = multiplet), integration, coupling constants [Hz]). IR data were obtained using an FT-IR with a flat CaF_2 cell. All measurements were recorded at 25 °C unless otherwise stated. Melting points are uncorrected. HRMS calculations were performed on an ESI-ion trap mass spectrometer. Compounds **3** and **6** were prepared according to literature procedures.[28,29] Spectral data were processed with ACD/NMR Processor Academic Edition.[30] Structure searches of the CSD were carried out using the ConQuest software.[31]

Compound Characterization. *in-12-Hydroxy-13-(1-methylethylidene)octahydro-1,4:5,8-dimethano-4a,8a-(methanoxymethano)naphthalene-9,11-dione (**1**).* To a flame-dried round-bottom flask equipped with a condenser and stir bar was added **10** (0.074 g, 0.26 mmol) in 4 mL of dry THF. To the solution was added a 2 M lithium borohydride solution (0.52 mL) in THF. The solution was then refluxed for 3 h. The solution was then quenched with a saturated solution of ammonium chloride and allowed to stir for an hour. The product was extracted into ethyl acetate, and the combined organic extracts were dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography with a 30% ethyl acetate and hexanes solution to yield **1** as white crystals (0.0099 g, 13% yield); mp = 167−171 °C; ^{1}H NMR ($CDCl_3$) δ 4.25 (d, 1H, J = 12.9 Hz), 4.05 (d, 1H, J = 13.1 Hz), 3.09 (m, 2H), 2.38 (s, 2H), 1.83 (d, 2H, J = 8.8 Hz), 1.78 (s, 6H), 1.74−1.64 (m, 4H), 1.45−1.38 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 173.7, 144.2, 125.3, 85.3, 70.2, 46.4, 42.0, 26.3, 24.7, 20.8; IR 3424, 3063, 2982, 1856, 1778 (cm^{-1}, CaF_2, CH_2Cl_2); HRMS (ESI+) calcd for $NaC_{17}H_{20}O_4$ 311.1253, found 311.1257.

*Dimethyl 7-(1-Methylethylidene)bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**3**):* Pale yellow solid, 93% yield; synthesized by following the synthetic route found in the literature.[28] Spectral and analytical data were in agreement with previous reports.

*Dimethyl 7-(1-Methylethylidene)bicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (**4**).* A solution of **3** (0.50 g, 2.01 mmol) dissolved in 20 mL of THF was treated with Wilkinson's catalyst (75 mg, 0.081 mmol). The mixture was shaken in a Parr apparatus under hydrogen at 3.2 bar for 2 days. The mixture was then filtered through Celite and concentrated under reduced pressure. The crude product was purified by flash chromatography on florisil with a 20% ethyl acetate and hexanes solution to yield **4** as a pale yellow oil, which solidified overnight into an amorphous solid (0.486 g, 96% yield): ^{1}H NMR ($CDCl_3$) δ 3.76 (s, 6H), 3.67 (m, 2H), 1.8 (d, 2H, J = 7.5 Hz), 1.53 (s, 6H), 1.38−1.28 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 165.1, 144.1, 112.1, 52.1, 45.3, 25.5, 19.7; IR 3063, 2956, 2873, 1727, 1618, 1436 (cm^{-1}, CaF_2, CH_2Cl_2); HRMS (ESI+) calcd for $NaC_{14}H_{18}O_4$ 273.1097, found 273.1097.

*8-(1-Methylethylidene)-4,5,6,7-tetrahydro-4,7-methanoisobenzofuran-1,3-dione (**5**).* To a stirred solution of **4** (1.31 g, 5.23 mmol) in 50 mL of THF at 0 °C was added lithium hydroxide monohydrate (1.10 g, 26.2 mmol) in 50 mL of water. The solution was allowed to warm to room temperature and continue stirring for an hour. The solution was then acidified with 3 M HCl and extracted with EtOAc (3 × 50 mL). The organic extracts were combined, dried with $MgSO_4$, and concentrated under reduced pressure to yield the carboxylic acid, which was used in the following step without further purification. The carboxylic acid was dissolved in 150 mL of trifluoroacetic anhydride and refluxed for 2 days. The solvent was distilled off, and the crude product was purified by flash chromatography on florisil with a 50% ethyl acetate and hexanes solution to yield **5** as a pale yellow oil, which solidified overnight into an amorphous solid (0.367, 34% yield) and was used as an intermediate in the synthesis of **7**: ^{1}H NMR ($CDCl_3$) δ 3.86 (s, 2H), 2.06−1.97 (m, 2H), 1.56 (s, 6H), 1.31−1.25 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 159.9, 158.2, 147.7, 115.1, 40.8, 25.4, 19.6; IR 2984, 2949, 2876, 1839, 1768, 1728 (cm^{-1}, CaF_2, CH_2Cl_2).

*1-(Cyclopenta-2,4-dien-1-yl)-1-methylsiletane (**6**):* Pale yellow liquid, 74% yield; synthesized by following the synthetic route found in the literature.[29] Spectral and analytical data were in agreement with previous reports.

*out-12-(1-Methylsiletan-1-yl)-13-(1-methylethylidene)-1,2,3,4,-5,8-hexahydro-1,4:5,8-dimethano-4a,8a-(methanoxymethano)-naphthalene-9,11-dione (**7**).* Anhydride **5** (1.28 g, 6.28 mmol) and silylated diene **6** (2.61 mL, 16 mmol) were combined with DCM (5 mL) in a capped 10 mL syringe. The resulting slurry was then pressurized for 2 days at 12 kbar. The resulting solution was concentrated under reduced pressure, and the residue was purified by silica gel flash chromatography with a 5% ethyl acetate and hexanes solution to yield **7** as white crystals (0.41 g, 18% yield): mp = 156−158 °C; ^{1}H NMR ($CDCl_3$) δ 6.36 (s, 2H), 3.28 (m, 2H), 3.11 (m, 2H), 2.82 (s, 1H), 2.03−1.88 (m, 2H), 1.69 (d, 2H, J = 10 Hz), 1.64 (s, 6H), 1.57−1.50 (m, 2H), 0.93−0.75 (m, 4H), 0.16 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 173.7, 142.7, 139.3, 119.5, 67.5, 51.8, 48.4, 42.2, 26.0, 20.7, 18.5, 14.9, −0.4; IR 2968, 2929, 2887, 1857, 1776, 1217 (cm^{-1}, CaF_2, CH_2Cl_2); HRMS (ESI+) calcd for $NaC_{21}H_{26}O_3Si$ 377.1543, found 377.1544.

*out-12-Hydroxy-13-(1-methylethylidene)-1,2,3,4,5,8-hexahydro-1,4:5,8-dimethano-4a,8a-(methanoxymethano)naphthalene-9,11-dione (**8**).* Compound 7 (0.41 g, 1.16 mmol) was dissolved in a 1:1 mixture of THF and methanol (50 mL) to which were added potassium fluoride (0.134 g, 2.31 mmol) and potassium bicarbonate (0.231 g, 2.31 mmol). The mixture was then cooled to 0 °C, and 30% hydrogen peroxide (1.96 mL, 17 mmol) was added dropwise. The solution was stirred overnight at room temperature. The solution was mixed with water to dissolve any salts and extracted once with ethyl acetate. The organic layer was washed with a 10% aqueous sodium sulfite solution. Aqueous layers were combined and extracted with ethyl acetate (3 × 50 mL). All organic extracts were combined, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography with a 30% ethyl acetate and hexanes solution to yield **8** as white crystals (0.29 g, 88% yield): mp = 174−177 °C; ^{1}H NMR ($CDCl_3$) δ 6.34 (s, 2H), 5.19 (s, 1H). 3.24 (m, 2H), 3.13 (m, 2H),

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2.19 (s, 1H), 1.68 (s, 6H), 1.68−1.64 (m, 2H), 1.50−1.42 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 172.3, 142.4, 135.2, 119.3, 83.7, 64.1, 54.1, 41.7, 25.7, 20.8; IR 3608, 3558, 3060, 2966, 2894, 1854, 1779 (cm^{-1}, CaF_2, CH_2Cl_2); HRMS (ESI+) calcd for $NaC_{17}H_{18}O_4$ 309.1097, found 309.1098.

*out-12-Hydroxy-13-(1-methylethylidene)octahydro-1,4:5,8-dimethano-4a,8a-(methanoxymethano)naphthalene-9,11-dione (**9**).* Compound **8** (0.450 g, 1.57 mmol) was added to a flame-dried three-neck round-bottom flask with large stir bar under nitrogen. Dipotassium azodicarboxylate (2.14 g, 11 mmol) was added, and the solids were dissolved in methanol (80 mL). Glacial acetic acid (1.26 mL, 22 mmol) was added dropwise to the stirred mixture. The mixture was allowed to stir until complete consumption of the starting material was observed by thin layer chromatography (2 h). The mixture was slowly quenched with water until gas evolution ceased. The product was extracted with ethyl acetate (3 × 30 mL), and the combined organic extracts were dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography on florisil with a 30% ethyl acetate and hexanes solution to yield **9** as white crystals (0.36 g, 79% yield): mp = 179−181 °C; ^{1}H NMR ($CDCl_3$) δ 5.28 (s, 1H), 2.97 (s, 2H), 2.41 (m, 2H), 2.05 (d, 2H, J = 9.2 Hz), 1.70 (s, 6H), 1.62−1.55 (m, 2H), 1.55−1.48 (m, 2H), 1.48−1.39 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 173.6, 143.3, 118.0, 76.7, 65.8, 47.1, 42.6, 25.7, 23.8, 20.9; IR 3612, 2972, 2895, 1854, 1777 (cm^{-1}, CaF_2, CH_2Cl_2); HRMS (ESI+) calcd for $NaC_{17}H_{20}O_4$ 311.1254, found 311.1254.

*13-(1-Methylethylidene)octahydro-1,4:5,8-dimethano-4a,8a-(methanoxymethano)naphthalene-9,11,12-trione (**10**).* To a flame-dried round-bottom flask equipped with a condenser and large stir bar were added **9** (0.10 g, 0.35 mmol), crushed 3 Å molecular sieves (0.89 g), and potassium carbonate (0.38 g). To the mixture was added DCM (20 mL) followed by cooling to 0 °C. PCC (0.094 g, 0.438 mmol) was added, and the solution was allowed to warm to room temperature before being refluxed overnight. The mixture was then filtered through Celite and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography with a 20% ethyl acetate and hexanes solution to yield **10** as white crystals (0.072 g, 72% yield): mp = 160−164 °C; ^{1}H NMR ($CDCl_3$) δ 2.99 (m, 2H), 2.26 (m, 2H), 1.87 (d, 2H, J = 10.8 Hz), 1.76 (d, 2H, J = 9.4 Hz), 1.68−1.6 (m, 4H), 1.60 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 205.4,172.1, 134.7, 129.8, 62.3, 45.1, 43.3, 25.1, 21.1, 19.4 ; IR 2988, 2893, 1863, 1781, 1764 (cm^{-1}, CaF_2, CH_2Cl_2); HRMS (ESI+) calcd for $NaC_{17}H_{18}O_4$ 309.1103, found 309.1106.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic specifications, NMR spectra, and molecular modeling parameters/atom coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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