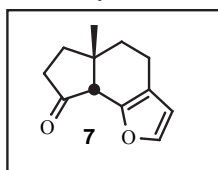


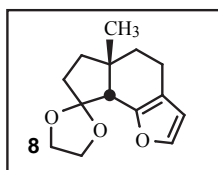
General Procedures. THF was distilled under a nitrogen atmosphere from sodium-benzophenone. TMSCl was distilled under argon from quinoline immediately before use, and Et₃N was distilled under argon from P₂O₅ and stored over KOH pellets. Both 1,1,3-trichloroacetone and 2,2,2-trifluoroethanol (TFE) were dried with Na₂SO₄/Na₂CO₃ and then distilled. Ethyl orthoformate was dried by distillation from sodium; ethylene glycol was dried by standing on 4A molecular sieves. Glassware was dried by either flaming under vacuum or storing in a 140° C oven for at least 24 h. Solutions of sodium trifluoroethoxide (NaTFE) were prepared by adding weighed and cleaned sodium pieces to an appropriate volume of TFE in a volumetric flask under argon, then diluting to the mark with TFE. NMR spectra were obtained on a Varian GEMINI2000 or Varian INOVA500 spectrophotometer using TMS as an internal reference. IR spectra were obtained as thin films between NaCl plates on a Perkin-Elmer 1600 series FTIR. The UFL Mass Spectroscopy Services performed high-resolution mass spectra.

Furanohydrindanone 7



To a 25-mL round bottomed flask was added magnesium turnings (134mg, 5.5 mmol) and a magnetic stirring bar. The flask and contents were flame dried under a rapid stream of dry argon. Upon cooling a crystal of I₂ was added and anhydrous THF (3 mL). The mixture was stirred rapidly and heated to 50° C. When the iodine color had faded (ca. 15 min), a solution of **5** (820 mg, 4.7 mmol) in anhydrous THF (7 mL) was added dropwise over 1.5 h; the temperature was maintained between 30-40° C. After the addition was complete, the mixture was cooled to room temperature and transferred via a cannula into a dry 25-mL round bottom flask. The mixture was then cooled in an ice-acetone bath (-10° C), and CuI was added (20 mg, 0.11 mmol). The mixture was stirred for 10 min, cooled to -78° C, and stirred for an additional 15 min. The mixture was then treated sequentially with TMSCl (1.8 mL, 14.2 mmol), Et₃N (2.0 mL, 14.3 mmol), and enone **4** (0.40 mL, 4.0 mmol). After stirring for 1 h at -78° C, the mixture was allowed to stand at 0° C for 18 h, stirred for 1 h at room temperature, and then poured into ice cold ether (50 mL)- saturated ammonium chloride (15 mL). The organic layer was removed, washed with saturated sodium hydrogen carbonate (15 mL) and saturated sodium chloride (15 mL), dried (Na₂SO₄), and evaporated to give a crude red oil (990 mg). The crude product was not purified, but characteristic signals in the ¹H NMR (300 MHz, CDCl₃) δ 0.21 (s, 9H), 1.70 (s, 3H), 2.42-2.80 (m, 4H), 4.52 (t, *J*=1.6 Hz, 1H), 6.26 (m, 1H), 7.2 (m, 1H), 7.34 (m, 1H) confirmed the existence of enol ether **6**. The crude product (490 mg) was taken up in 170 mL of a 0.30 M solution of LiClO₄ in 4:1 MeCN:*i*-PrOH. 2,6 Lutidine (0.90 mL, 7.7 mmol) was then added. The mixture was placed in a 1.0-L beaker and a steel cathode, carbon anode and Ag/AgNO₃ reference electrode were inserted into the solution. A constant current of 100 mA was passed through the solution until 350 coulombs of charged had been delivered. The volatiles were removed in vacuo and the residue was partitioned between water (20 mL) and ethyl acetate (25 mL). The aqueous layer was extracted with ethyl acetate (3 X 10 mL); the combined extracts were washed with 1N HCl (20 mL), saturated sodium chloride (20 mL), dried (MgSO₄) and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (7:1 hexanes: ethyl acetate) to provide **7** as a pale yellow oil (244 mg, 65% based on **4**). IR 2930, 1745, 1550, 1050, 900 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.19 (s, 3H), 1.52-1.88 (m, 3H), 2.0 (dt, *J*= 3.0, 12.4 Hz, 1H), 2.41 (dt, *J*= 2.5, 12.3 Hz, 1H), 2.5 (m, 1H), 3.0 (s, 1H), 6.21 (d, 1.9 Hz, 1H), 7.35 (d, 1.9 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 19.0, 25.5, 31.7, 33.1, 35.5, 40.2, 54.9, 110.0, 116.7, 142.6, 144.7, 215.1; HRMS (EI) *m/z* (M⁺) calculated for C₁₂H₁₄O₂, 190.0994, found: 190.0993.

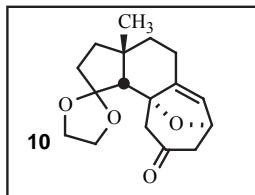
Ketal 8



Ketone **7** (167 mg, 0.88 mmol) was placed in a 5-mL pear shaped flask equipped with a magnetic stirring vane. Ethylene glycol (0.600 mL), ethyl orthoformate (0.150 mL, 0.90 mmol), and *p*-TsOH•H₂O (17 mg, 0.09 mmol) were added and the mixture was stirred at room temperature for 8 h. Saturated sodium bicarbonate (2 mL) was added, and the mixture was extracted with ether (5 X 3 mL). The combined extracts were washed with brine (5 mL), dried (Na₂SO₄), and concentrated. The crude product was purified by flash chromatography on silica gel (9:1 hexanes: ethyl acetate) to provide **8** as a pale yellow oil (144 mg, 70%). IR 3018, 2931, 1560, 1216, 1080, 950 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.05 (s, 3H), 1.38 (dt, *J*=3.8, 14.4 Hz, 1H), 1.58-1.76 (m, 2H), 1.85 (ddd, *J*=2.8, 4.5, 6.9, 1H), 2.04 (t, *J*= 7.8 Hz, 2H), 2.4-2.5 (m, 2H), 2.75 (s, 1H), 3.61 (ddd, *J*=0.9, 6.4, 7.1 Hz,

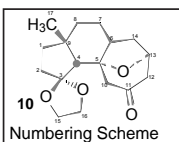
1H), 3.81 (ddd, $J = 1.4, 6.4, 6.4$ Hz, 1H), 3.89 (ddd, $J = 1.4, 6.2, 7.1$ Hz, 1H), 4.10 (ddd, $J = 0.9, 6.4, 6.2$ Hz, 1H), 6.26 (d, $J = 1.9$ Hz, 1H), 7.28 (d, $J = 1.9$ Hz, 1H); ^{13}C NMR (75MHz) δ 19.5, 25.9, 32.4, 36.0, 36.8, 41.3, 53.3, 64.3, 65.2, 110.2, 117.3, 117.5, 141.1, 148.4; HRMS (EI) m/z (M^+) calculated for $\text{C}_{14}\text{H}_{18}\text{O}_3$, 234.1256, found: 234.1245.

Cycloadduct 10



A 5-mL pear shaped flask equipped with a magnetic stirring vane was charged with a solution of ketal **8** (5 mg, 0.021 mmol) in TFE (0.200 mL). To this stirred solution was added 1,1,3 trichloroacetone (0.007 mL, 0.066 mmol) in TFE (0.036 mL) and a 1.9 M solution of NaTFE/TFE (0.068 mL, 0.13 mmol NaTFE) over 2.5 h at room temperature. Stirring was continued for 0.5 h; the mixture was then diluted with saturated brine (1.0 mL) and CH_2Cl_2 (2.0 mL). Water was added until all the solids were dissolved (ca. 0.5 mL). The aqueous phase was

extracted with CH_2Cl_2 (4 X 1.5 mL); the combined extracts were washed with saturated sodium chloride (3 mL), dried (MgSO_4) and concentrated. The residue was dissolved in methanol saturated with NH_4Cl ; Zn/Cu couple was added (50 mg) and the mixture was stirred at room temperature for 18 h. The mixture was then filtered through a pad of celite, diluting with ethyl acetate (10 mL) in the process. The volatiles were removed in vacuo, and the residue was partitioned between water (2 mL) and ethyl acetate (4 mL). A saturated aqueous solution of Na_2EDTA was added (ca. 0.50 mL) to break the emulsion. The aqueous phase was extracted with ethyl acetate (4 X 2 mL); the combined extracts were washed with saturated sodium chloride (4 mL), dried (MgSO_4) and concentrated. The crude product was purified by flash chromatography on silica gel (gradient elution 10:1 \rightarrow 3:1 hexanes: ethyl acetate) to provide starting material **8** (1 mg, 0.003 mmol) and ketone **10** as a white solid (4 mg, 66%, 83% based on recovered starting material). IR 2929, 1741, 1501, 1405, 1023, 874 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.16 (s, 3H), 1.32 (dt, $J = 5.3, 13.6$ Hz, 1H), 1.54 (ddd, $J = 7.4, 9.4, 13.0$ Hz, 1H), 1.64 (dt $J = 7.7, 13.0$ Hz, 1H), 1.80 (ddd, $J = 4.7, 11.0, 13.6$ Hz, 1H), 1.86 (dd, $J = 7.4, 14.1$ Hz, 1H), 1.90 (ddd, $J = 2.4, 7.5, 13.7$ Hz, 1H), 2.11 (s, 1H), 2.25 (ddd, $J = 5.3, 11.0, 16.4$ Hz, 1H), 2.25 (d, $J = 16.3$ Hz, 1H), 2.51 (dt, $J = 5.1, 16.4$ Hz, 1H), 2.55 (d, $J = 16.0$ Hz, 1H), 2.67 (d, $J = 16.0$ Hz, 1H), 2.73 (dd, $J = 5.1, 16.2$ Hz), 3.78 (q, $J = 6.9$ Hz, 1H), 3.83 (q, $J = 6.5$ Hz, 1H), 3.86 (td, $J = 6.6, 4.6$ Hz, 1H), 4.06 (ddd, $J = 4.0, 5.6, 6.4$ Hz, 1H), 4.94 (d, $J = 5.0$ Hz, 1H), 5.62 (m, 1H); ^{13}C (126 MHz, CDCl_3) δ 21.9, 28.5, 30.7, 32.7, 36.8, 37.3, 40.3, 45.9, 54.0, 57.6, 64.8, 65.4, 76.5, 83.8, 118.4, 120.5, 145.6, 206.9; HRMS (EI) m/z (M^+) calculated for $\text{C}_{17}\text{H}_{22}\text{O}_4$, 290.1518, found: 290.1498



^{13}C and ^1H NMR Assignments for 10

C	^{13}C δ	^1H δ
1	37.3	α 1.64, β 1.54
2	36.8	α 1.86, β 1.90
3	119.4	-
4	57.6	2.11
5	83.8	-
6	145.6	-
7	21.9	α 2.51, β 2.25
8	32.7	α 1.80, β 1.32
9	40.3	-
10	54	α 2.55, β 2.67
11	206.9	-
12	45.9	α 2.73, β 2.25
13	76.5	4.94
14	120.5	5.62
15	64.8	α 4.06, β 3.78
16	65.4	α 3.83, β 3.86
17	28.5	1.16